PHYSICAL REVIEW B VOLUME 49, NUMBER 7 15 FEBRUARY 1994-I

Initial stages of Ge/GaAs(100) interface formation

X.-S. Wang,* K. Self, V. Bressler-Hill, R. Maboudian,† and W. H. Weinberg
Center for Quantized Electronic Structures (QUEST) and Department of Chemical Engineering, University of California, Santa Barbara, California 93106
(Received 9 September 1993)

The initial stages of formation of the Ge/GaAs(100) interface have been investigated by monitoring, using low-energy electron diffraction and scanning tunneling microscopy (STM), the structural changes of the GaAs(100) surface after submonolayer germanium deposition and annealing. The distribution of Ge atoms on the GaAs(100)-(2 × 4) surface is random when the substrate temperature is below 600 K. After annealing at about 700 K, a poorly ordered (2 × 1) LEED pattern is observed which is attributed to Ge-As dimerization. When annealed above 825 K, a well-ordered, stable surface with a (1 × 2) superstructure is obtained, suggesting the formation of Ge-Ga dimer bonds. These results demonstrate the usefulness of STM in monitoring changes in the interfacial atomic structures during the initial stages of heteroepitaxy, which is an essential step in understanding and controlling other important interfacial properties, such as energy band offset.

I. INTRODUCTION

The atomic structure of the interface between two dissimilar semiconductors is one of the most important factors influencing the electronic characteristics of heterostructures. In particular, recent experimental and theoretical studies have revealed that the energy band offset across a heterojunction is closely related to the atomic configuration at the interface[1–5]. By inserting a few monolayers of a third type of semiconductor at the interface, the band offset can be adjusted,[6–8] e.g., AlAs-Ge-GaAs. Furthermore, a band offset can be created by adding atomic interlayers at a homojunction, such as GaAs-Ge-GaAs[9] and Ge-GaAs-Ge[10]. The tunability of the band offset is expected to lead to new schemes for developing novel electronic materials and devices.[11] One significant deterrent to this development is the limited knowledge available concerning the atomic structure at a semiconductor interface, even in the case of nearly lattice-matched materials such as Ge/GaAs(100).[12–18]

We report here low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) studies of atomic structures in the initial stages of Ge/GaAs(100) interface formation. Although this prototypical IV/III-V semiconductor interface has been investigated extensively,[1,2,12–18] there is no consensus regarding the atomic configuration at the interface. Some observed that the surface reconstruction changed from a (2 × 4) to a mixture of (1 × 2) and (2 × 1) at the beginning of Ge epitaxial growth on GaAs(100),[15,18] while others found a single phase of (1 × 2) (Ref. 14) or (2 × 1) (Ref. 16) superstructures after deposition of a few monolayers of germanium. Our results show that the distribution of a submonolayer of Ge atoms deposited on the GaAs(100) surface at a substrate temperature below 600 K is random. However, after annealing at 700 K, a poorly ordered (2 × 1) structure forms on the surface, and, with further annealing at 875 K, a well-ordered (1 × 2) superstructure is observed. These results are explained by the formation of Ge-As and Ge-Ga dimers on the surface.

II. EXPERIMENTAL PROCEDURES

Both *n*-type (Si-doped) and *p*-type (Be-doped) high conductivity ($\sim 5\times10^{17}$ cm^{-3}) nominally flat GaAs(100) substrates were employed. The (2 × 4) reconstructed clean GaAs(100) surface was prepared by a standard molecular beam epitaxy (MBE) growth procedure.[19] The samples were then transferred by means of a portable ultrahigh vacuum (UHV) interlock[20] to a separate surface analysis chamber. The surfaces were analyzed by LEED, Auger electron spectroscopy (AES), and STM. A thermal evaporator containing high purity germanium was used for Ge deposition, and the overlayer coverage was estimated from AES measurements. Specimens were annealed from the backside by a hot filament. In order to be able to change samples *in situ*, good thermal contact between the thermocouple and the sample was unattainable. Hence, we calibrated the thermocouple and estimated the error using an infrared pyrometer, and reference temperatures of the indium melting point at 429 K and the aluminum-silicon eutectic point at 850 K. The reported temperatures are accurate to approximately ± 25 K.

III. RESULTS AND DISCUSSION

The MBE-grown, UHV-transferred GaAs(100) samples were free of contamination, as judged by AES. A STM image of clean GaAs(100) with the As-rich (2 × 4) surface reconstruction is shown in Fig. 1(a). It is well known that bulk-terminated semiconductor surfaces, like the model in Fig. 2(a) for GaAs(100), are not stable due to the high density of dangling bonds, and they reconstruct in order to lower their surface energy.[21] Our atom-resolved images show that the (2 × 4) structure produced under our growth conditions consists of two As dimers and two missing dimers in each reconstructed unit cell.[22] A structural model consistent with the images of the GaAs(100)-(2×4) surface is shown in Fig. 2(b).[23] The top layer consists of two As-As dimers in each (2×4) unit cell,

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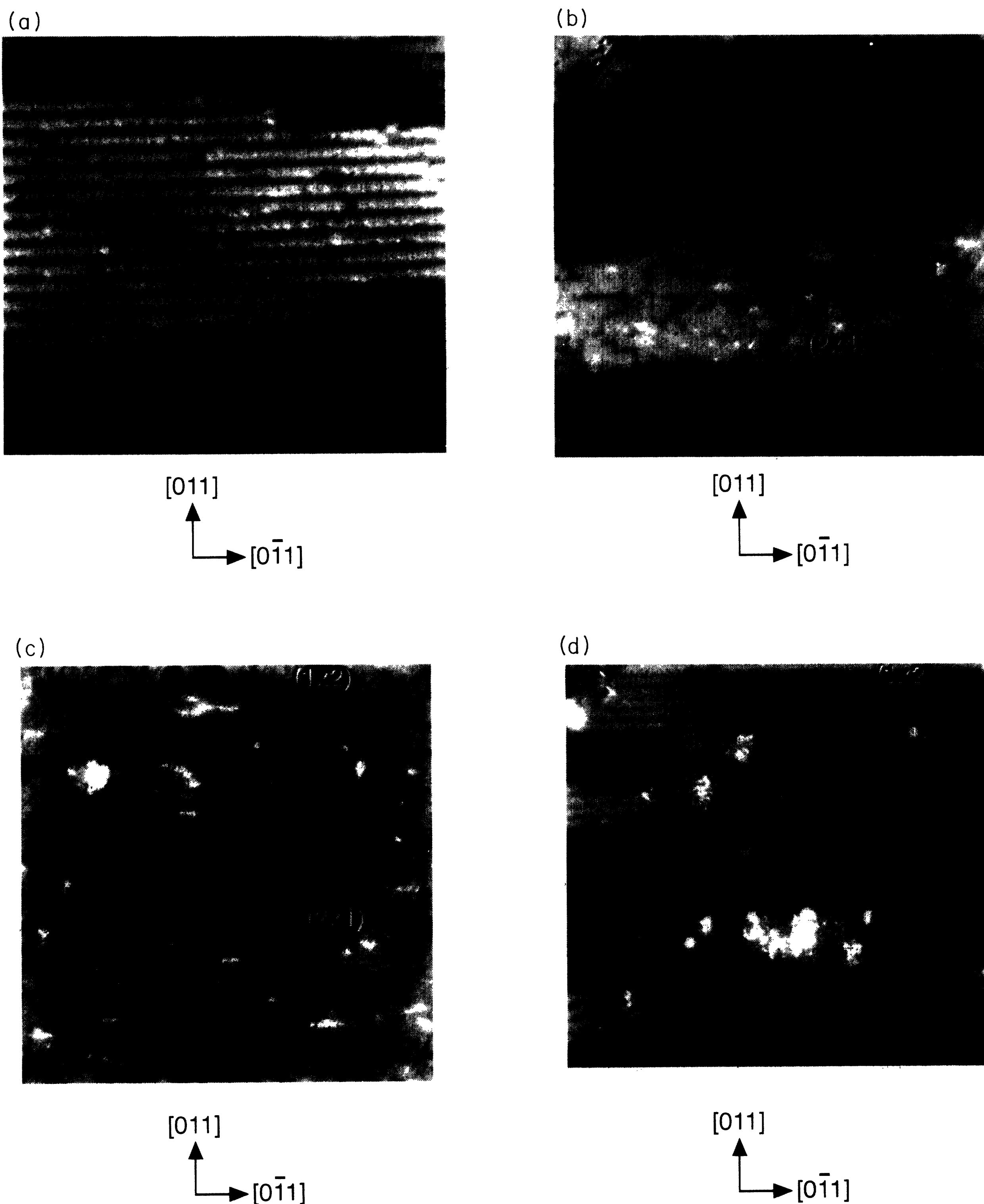

FIG. 1. Gray scale STM images of (a) the clean MBE-grown GaAs(100)-(2×4) surface; (b) the surface after Ge deposition at a substrate temperature of 600 K [note the degradation of the (2 × 4) reconstruction]; (c) the poor (2 × 1) order formed after annealing at 700 K; and (d) the (1 × 2) superstructure and the amorphous domains formed after annealing at 875 K. The size of the imaged area in all cases is 370 × 370 Å^2, and the gray scale is about 5 Å. These images were measured at −2.4 V sample bias and a constant current of 0.15 nA. The imaged areas in both (a) and (b) include an island which is 2.8 Å above the terrace.

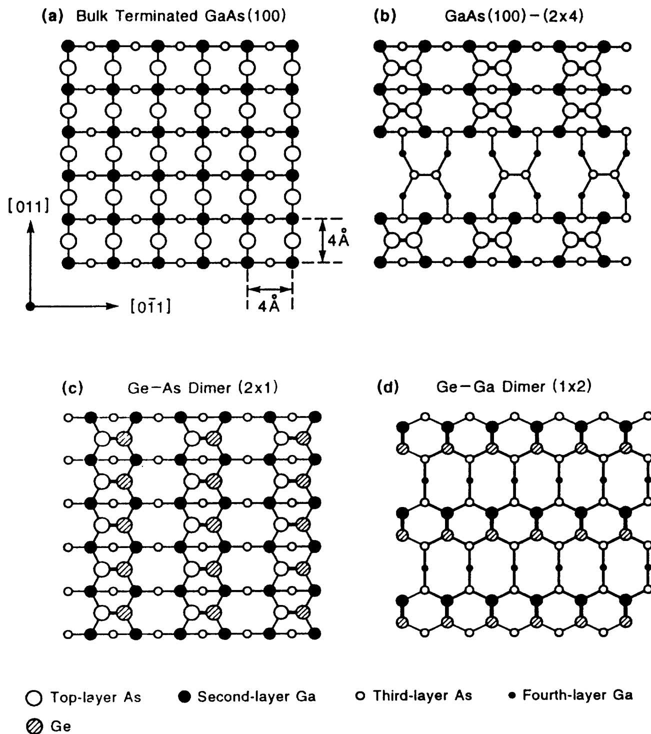

FIG. 2. Surface structural models for (a) bulk-truncated GaAs(100) surface with an As-top layer; (b) As-rich (2 × 4) reconstructed GaAs(100) (Ref. 23); (c) Ge-As dimerization forming a (2 × 1) superstructure on GaAs(100); and (d) the (1 × 2) order formed by Ge-Ga dimerization.

forming rows along the [01̄1] direction that are spaced by 16 Å in the [011] direction. The two second-layer Ga atoms that would have been located in the missing dimer row are missing, and this allows the two As atoms in the third layer to dimerize. After a submonolayer of germanium was deposited at a substrate temperature of 600 K, the (2 × 4) LEED pattern became diffuse. The coverage was measured using AES, which is, unfortunately, an insufficient tool for a more accurate determination of the coverage. STM images, cf., Fig. 1(b), still show the existence of (2 × 4) rows, but now many defects are observable, and the long-range order of the (2 × 4) superstructure has degraded noticeably. The distribution of Ge atoms on the surface appears random, but quite uniform. In contrast to the results of Yang *et al.*[24] for Ge deposition on GaAs(110), neither cluster formation nor preferential nucleation at step edges occurred on the GaAs(100)-(2 × 4) surface, which suggests that the Ge atoms are immobile on this surface at the deposition temperature of 600 K.

After annealing surfaces like those of Fig. 1(b) at 700 K for 5 min, we observed that the 4× reconstruction in the [011] direction in the LEED pattern disappeared totally, and only weak 2× order in the [01̄1] azimuth remained. As may be seen in Fig. 1(c), STM scans reveal the dominant surface structures are rows along the [011] direction which correspond to the poor (2×1) order of the surface. These rows usually extend less than 100 Å, and the spacing between them is normally 8 Å. In addition to the (2 × 1) superstructure, small regions of the original (2 × 4) structure and rows (8 Å in width) along the [01̄1] direction can be observed. The (2×1) and (2×4) features appear on the same vertical level, while the rows along the [01̄1] direction are either 1.4 Å higher or lower.

The LEED pattern changed from a weak (2×1) to a diffuse (1×1) after the sample was annealed to 750 K. With STM, we observed that the (2 × 1) rows along the [011] direction disappeared almost totally, leaving disordered features on the surface. Furthermore, additional rows along the [01̄1] direction beneath the top layer became visible. When the sample was annealed above 825 K, however, a (1 × 2) LEED pattern emerged. This pattern became quite sharp after 5 min of annealing at 875 K, and no (2 × 1) order remained visible. The STM images of this surface show domains of well-ordered (1 × 2) superstructure, as is evident in Fig. 1(d). The (1×2) phase consists of 8 Å spaced rows stretching over relatively long distances along the [01̄1] direction. The individual (1×2) unit cells were resolved, and, in addition, islands with 2.8 Å steps and the same (1 × 2) superstructure could be found frequently. Occasionally, we have observed regions with a few consecutive layers of the (1 × 2) reconstruction. Some (2 × 1)-like rows could also be observed at vertical levels of 1.4 Å higher or lower than the (1 × 2) terraces, but they were rather short (< 50 Å) and did not form domains of any significant size. They appear to be metastable structures that disappear after further annealing. The surface area between the (1 × 2) domains was found to be amorphous, but smooth.

These results cannot be explained simply as either the structure of the GaAs(100) or Ge(100) surface. While the 2.8 Å GaAs bilayer steps are present on the GaAs(100) surface, the (1 × 2) and (2 × 1) structures do not exist.[25] On nominally flat Ge(100) surfaces, approximately equal-sized domains of (1 × 2) and (2 × 1) order are observed, which are separated by 1.4 Å steps.[26] In theoretical studies of Ge-GaAs polar heterojunctions, Harrison *et al.*[12] demonstrated that electrostatic energy was an important factor in determining the interfacial atomic configuration. In the case of Ge on GaAs(100), an abrupt junction would have a large interfacial charge accumulation, which would increase the potential energy of the system enormously. A mixed layer of half Ge and half As, or half Ge and half Ga, however, produces an interface that is uncharged with a dipolar layer which shifts the bulk potential by a finite amount.[12,13] Based on these observations and our experimental results, we propose the following structural model for the GaAs(100) surface with submonolayer concentrations of germanium: Ge atoms form dimers with surface As and Ga atoms, creating the (2×1) and (1×2) superstructures which are shown in Figs. 2(c) and 2(d), respectively. The alignment of the individual dimers in Figs. 2(c) and 2(d) is not intended to exclude the possibility of other dimer-dimer configurations (e.g., alternating or random) which could occur. When the sample is annealed to 700 K, Ge atoms form dimers with the top-layer As atoms. Since arsenic desorption occurs at this temperature,[25] the As atoms needed to form a complete (2 × 1) Ge-As dimer layer are gradually disappearing.

Moreover, the Ga atoms in the second layer, according to Chadi,[23] have a coverage of 75%, which is insufficient to support a complete (2×1) top layer. These factors allow only a poorly-ordered (2×1) surface to be observed. When the surface is annealed at higher temperatures, arsenic continues to desorb, and eventually the top-layer As atoms (even those dimerized with Ge atoms) are removed from the surface. The Ge atoms then begin to form dimers with the original second-layer Ga atoms, and this results in a surface with (1×2) order. Based on a Ge-Ga dimer model, the surface composition of the (1×2) domains is only 50% Ga. Since the second layer coverage of Ga was 75% in the original (2×4) reconstruction, it seems likely that the amorphous regions separating the (1×2) domains are Ga rich.

Previously, single phases of both (1×2) and (2×1) order have been reported for the Ge/GaAs(100) interface. Using reflection high-energy electron diffraction, a (2×1) pattern was observed by Banerjee *et al.*,[16] when they deposited a few atomic layers of Ge on GaAs(100)-(2×4) at 700 K, presumably under the As over-pressure condition of MBE growth. When Ge deposition was performed in an UHV environment on a GaAs(100) surface held above 673 K, Mrstik[14] observed a sharp (1×2) LEED pattern, with the Ge coverage in the range of 0.2–4 monolayers. Similar LEED studies have found that Si monolayers deposited at 875 K on both initially As- and Ga-rich GaAs(100) surfaces formed a (1×2) superstructure.[27] These results suggest that As atoms are required in the top layer to form the (2×1) superstructure, and the top layer of the (1×2) superstructure consists of Ga and Ge atoms. Our STM images show that the (1×2) and (2×1) structures appear at vertical levels equivalent to those of the Ga and As atomic layers of the GaAs(100) surface. The ordered Ge-Ga and Ge-As arrangements yield favorable electronic structures that enhance the thermodynamic stability of the surfaces. Applying electron counting arguments,[28] it is found that there are four electrons remaining for each (1×2) Ge-Ga surface unit cell, assuming that the second layer consists only of As atoms. The surface electronic structure would then be similar to that of the dimerized Si(100) surface,[29] i.e., two electrons form the σ-dimer bond, and the other two occupy a delocalized π bonding orbital. The Si(100)-(2×1) surface is thermodynamically stable: the dimer phases can be observed at a temperature above 1375 K.[30] We have found that the well-ordered Ge-Ga (1×2)/GaAs(100) surface can sustain annealing above 900 K. No phase exists on the clean GaAs(100) surface at this temperature that maintains such order,[25] i.e., the ordered Ge-Ga dimer layer appears to prevent the loss of subsurface arsenic at high temperatures.

The dipole moment at the interface is expected to change the band offset of a heterojunction, i.e., the so-called dipolar shift.[12] The direction and magnitude of this shift are determined by the interfacial atomic structure. Therefore, in addition to the bulk properties of the semiconductors, the band offset of a heterojunction is closely related to the detailed atomic configuration at the interface.[2–8] Our results show that an overlayer with a finite dipole density can be stable, and that the atomic structure proposed in Ref. 12 involving more transition layers to achieve zero dipole has not been observed. Our results also demonstrate clearly that different interfacial atomic configurations can be realized by choosing proper epitaxial growth conditions. Theoretically, for the Ge-GaAs(100) heterojunction, the difference in band offset between the $\frac{1}{2}$(Ge + Ga) and $\frac{1}{2}$(Ge + As) interface is about 0.6–0.7 eV.[12,13] Experimentally, such a large band offset has been observed across GaAs-AlAs(100) hetrojunctions with a Ge interlayer.[6,8] This variation was explained by a dipolar shift at the interface of the III-V/IV/III-V structures,[8] and not by net charge accumulation at the heterojunctions,[6] consistent with our proposed surface structures.

IV. SUMMARY

In summary, dramatic structural changes have been observed on the GaAs(100) surface after submonolayer Ge deposition and annealing. A poorly ordered (2×1) and a well-ordered (1×2) superstructure are formed after 700 K and 875 K annealing, respectively. These surface structures can be described by the formation of Ge-As and Ge-Ga dimers. These adjustments of the interfacial atomic structures are at the foundation of heterostructure band offset engineering.

ACKNOWLEDGMENTS

We wish to thank D. Leonard for the MBE sample growths, P. Petroff for helpful discussions, and J. English and M. Wassermeier for technical assistance. This work was supported by QUEST, a National Science Foundation Science and Technology Center (Grant No. DMR 91-20007), the W. M. Keck Foundation, and a MICRO-SBRC Grant.

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*Present address: Department of Materials Science and Chemical Engineering, University of Minnesota, Minneapolis, MN 55455.

†Present address: Department of Chemical Engineering, University of California, Berkeley, CA 94720.

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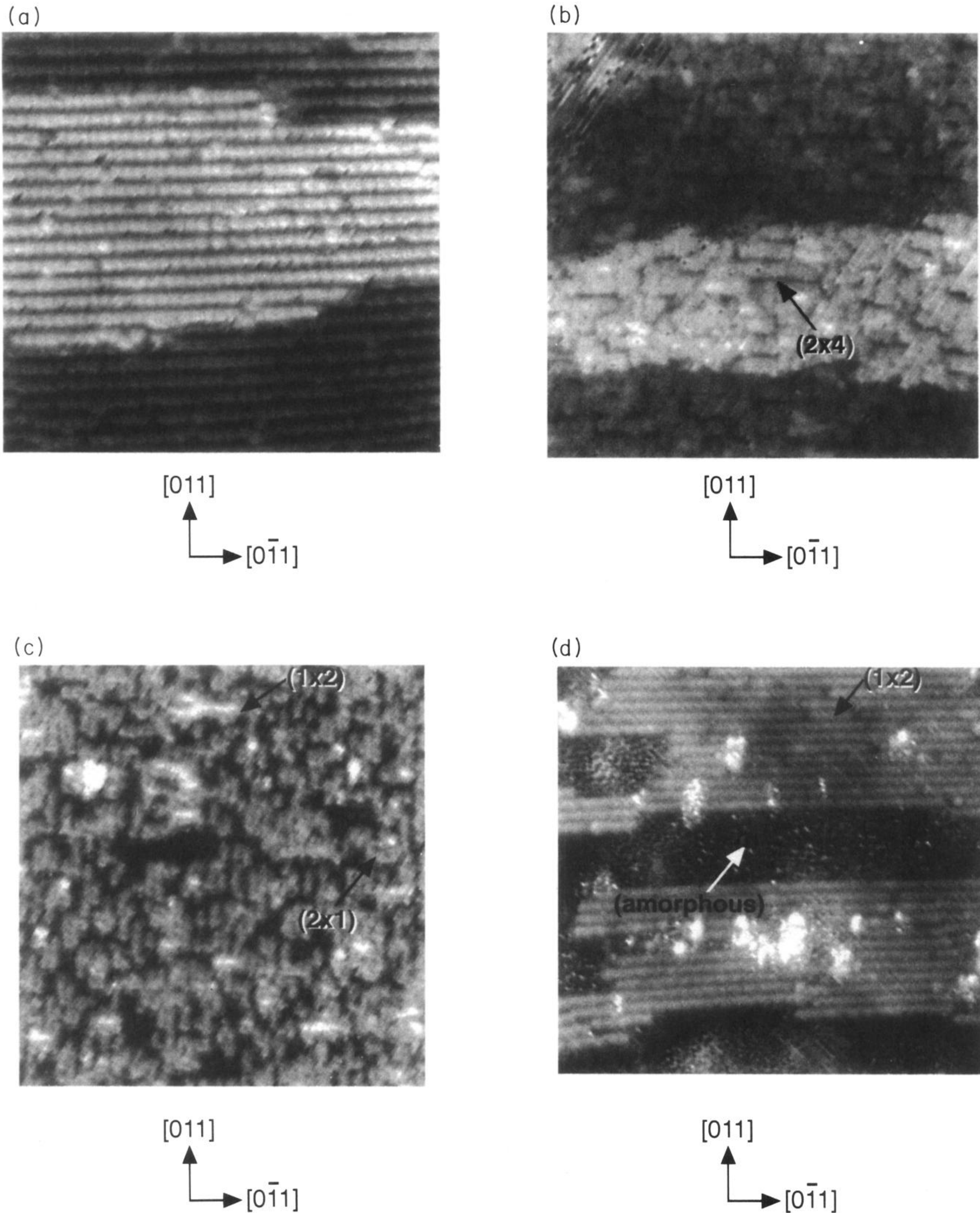

FIG. 1. Gray scale STM images of (a) the clean MBE-grown GaAs(100)-(2×4) surface; (b) the surface after Ge deposition at a substrate temperature of 600 K [note the degradation of the (2 × 4) reconstruction]; (c) the poor (2 × 1) order formed after annealing at 700 K; and (d) the (1 × 2) superstructure and the amorphous domains formed after annealing at 875 K. The size of the imaged area in all cases is 370 × 370 Å^2, and the gray scale is about 5 Å. These images were measured at -2.4 V sample bias and a constant current of 0.15 nA. The imaged areas in both (a) and (b) include an island which is 2.8 Å above the terrace.