Atomic-scale surface structure and ultrasmooth morphology of molecular-beam-epitaxy-grown AlAs (001)-(3×2)

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We have studied the surface atomic structure and electronic properties of the molecular-beam-epitaxy-grown AlAs(001)-(3×2) film by in situ scanning tunneling microscopy and spectroscopy. A structural model is proposed for AlAs(001)-(3×2), in which the ×2 ordering arises from the formation of unusual double π-bonded As dimers along the [110] direction and the ×3 ordering results from the missing As-dimer rows in the [110] direction on the topmost As-terminated layer. Scanning tunneling spectroscopic study directly reveals the energies and spatial locations of the surface states. [S0163-1829(97)52204-1]

For the epitaxial growth of semiconductors it is known that surface reconstruction plays a critical role in the growth processes and the resulting surface morphology, stoichiometry, and other properties of the grown films. Differently reconstructed surfaces usually have special kinds of dimers with unique bond structures. Surfaces with different reconstructions, even different phases of a same reconstruction, have drastically different growth behavior, and must be understood very well for controlling the epitaxial growth processes. In situ scanning tunneling microscopy (STM),1–5 with its unprecedented ability to obtain the real-space atomic-scale information on the growth surfaces, is a particularly suitable approach for this purpose because the significance of surface reconstruction for the growth processes on a microscopic scale can be explored.

In this paper we address on the surface structure of AlAs(001). Because the lattice parameter difference between GaAs and AlAs is very small, high-quality AlAs/GaAs or AlxGa1−xAs/GaAs multilayered structures can be readily made using modern epitaxial growth techniques. However, the ultimate performances of AlxGa1−xAs/GaAs based devices are still critically dependent on the abruptness and smoothness of the heterointerfaces. While in most cases the topology of the interface can be tailored by selecting the proper growth conditions and growth techniques such as growth interruption6 and migration enhanced epitaxy, the quality of the interface is inevitably impaired by the intrinsic properties of the grown materials. Especially for the growth of AlxGa1−xAs by molecular-beam epitaxy (MBE) with a large Al content, it is often complicated by the appearance of rough surface morphology under typical growth conditions. For a given set of growth conditions there is a range of intermediate substrate temperatures, a so-called ‘‘forbidden window,’’ where rough growth of AlxGa1−xAs is observed.8–10 In the past, the interpretations of this phenomenon have been mainly attributed to the fact that Al adatoms have higher chemical reactivity and slower surface migration compared with that of Ga adatoms under the same growth conditions, therefore resulting in the much rougher growth morphology. Recently, based on their reflection high-energy electron diffraction (RHEED) study, Dabiran et al. suggested that the reconstructions of AlAs(001) at different sample temperatures are crucial in the growth process of AlAs.10 In their work, reentrant two-dimensional (2D) layer-by-layer growth modes of AlAs were found to coincide closely with the onsets of surface reconstruction transitions at both high [(2×4)→(3×2)] and low [c(4×4)→(2×4)] sample temperatures.

We report here a direct determination of the detailed surface structure and electronic properties of the high-temperature grown (HTG) AlAs(001)-(3×2) using in situ STM and scanning tunneling spectroscopy (STS). An atomic model of HTG AlAs(001)-(3×2), which contains unusual double π-bonded As dimers, is proposed based on our STM data. The experiments were performed in an ultra-high-vacuum (UHV) MBE/STM system. The base pressure of this multiple-chamber system during the experiments was better than 6.0×10−11 Torr. The sample substrates used in our experiments were cut from a nominally singular GaAs(001) wafer (Zn-doped, miscut angle less than 0.2°). Initially, a 10-bilayer (BL; i.e., Al+As) AlAs buffer was grown on top of a thick GaAs buffer at a growth temperature of 600 °C to serve as a protective layer of the underlying GaAs film against subsequent high-temperature annealing/growth.10 Later, the AlAs buffer layer was annealed at 700 °C under the As flux for a few minutes to obtain the 3×2 reconstructed phase. At this point, the substrate temperature was lowered to 690 °C and the 10-BL HTG AlAs layer started to grow. During and after the MBE growth process, the HTG AlAs(001) surface displayed a sharp and streaky 3×2
RHEED pattern, indicating a smooth growth morphology. The RHEED intensity oscillations were recorded during the growth of AlAs with the electron beam at an azimuthal angle along the [110] direction and at an electron energy of 8 keV. The epilayers were doped by Si atoms during the MBE growth at a concentration of \( \approx 6 \times 10^{17} \text{cm}^{-3} \).

STM measurements were performed in the constant-current mode and chemically etched tungsten tips were used. The typical surface morphology of the HTG AlAs(001)-(3 \times 2) is extremely smooth, as shown in Fig. 1(a), on a completely relaxed surface of a 10-BL film obtained by a short annealing after MBE growth. Figure 1(b) shows a RHEED specular-beam intensity oscillation curve recorded during the growth of HTG AlAs(001). Figure 2(a) shows an example of typical high-resolution STM topographs obtained on the AlAs(001)-(3 \times 2) surface at a sample bias voltage of \(-3.5\) V, which reveals two types of topographic maxima (the topographic corrugation is \( \approx 0.1–0.2 \text{ Å} \)): type-I sites (illustrated by yellow dots), displaying a \( \times 2 \) periodicity due to the dimerization along the [110] direction and a \( \times 3 \) periodicity along the [110] direction; and type-II sites (illustrated by blue dots), having a \( \times 1 \) periodicity along the [110] direction and a nearly \( \times 1 \) periodicity along the [110] direction except regions overlapped with the type-I sites. In our study, we found a strong bias-voltage-dependent imaging behavior. In the filled-state STM topographs at low tunneling bias voltages, both type-I and type-II sites can be imaged simultaneously. However, when tunneling bias was increased to higher values (>\( 4.0 \text{ V} \)), only rows of type-I sites can be imaged [see the inset of Fig. 2(a)]. Also, the type-I dimerized row feature completely disappeared while the type-II feature remains the same in the STM topographs (not shown here) obtained on the AlAs(001)-(3 \times 2) surfaces annealed at the same temperature but under As-flux-deficient conditions, suggesting a strong chemical bonding difference between type-I and type-II sites. From the bias-voltage and annealing-flux dependent STM imaging mentioned above, we conclude that two types of topographic sites should correspond to positions of both cations and anions atoms in the topmost bilayer and the type-I sites should be related to the topmost surface atoms because of its dimerization nature.

The important question to be resolved next is whether the type-I sites correspond to anion positions (As-terminated surface) or cation positions (Al-terminated surface). Since the orientation of the As bonds was already confirmed from the orientation of the imaged As-dimer rows of the As-terminated GaAs(001)-(2 \times 4) and AlAs(001)-(2 \times 4) surfaces grown on the same substrate using STM, the only possibility to satisfy the observed registry of top surface dimers and underlying atoms as shown in the high-resolution STM images is on an As-terminated surface [see Figs. 2(a) and 2(b)]. Based on the high-resolution STM data, we could construct a tentative surface structural model. Figure 2(c) shows this model, which includes the following important features: (1) double \( \sigma \)-bonded As-dimer rows running along the [110] direction, (2) in the [110] direction, two missing As-dimer vacancy rows alternating with one As-dimer row, and (3) unreconstructed or slightly relaxed (undetectable by STM) exposed Al atoms of the first underlying layer.

To understand further the surface electronic structure and the origin of the bias-voltage-dependent imaging behavior, we have also performed tunneling spectroscopic measurements. Figure 3 shows the averaged normalized tunneling conductance spectra of the AlAs(001)-(3 \times 2) surface measured at two tip-sample separations (\( S_1 < S_2 \)). We only display the filled-state portions of the spectra since the density of empty surface states is too low to be detected with our instrumentation setup under these tunneling conditions. The normalized tunneling conductance is used here because it has been shown to be a good approximation to the local density of surface states.\(^\text{11}\) Two most prominent normalized conductance structures located at \(-2.2 \pm 0.1 \text{ eV} (A)\) and at \(-3.6 \pm 0.1 \text{ eV} (B)\) below the Fermi level can be clearly seen in the tunneling spectra. Also, structure A shows a much stronger dependence on the tip-sample separation compared with structure B as can be seen from the relative peak ratios at different tip-sample separations, implying a different decay behavior into the free space of the related surface state wave functions. At some larger tip-sample separations (exact threshold value will depend on the specific tunneling probe used), we could also observe a complete dominance of structure B in the tunneling spectra.

Because the relative tunneling probability of the \( B \) states, compared to tunneling from the \( A \) states which are closer to the Fermi level, is much reduced because of a higher effective tunneling barrier, it is also necessary to examine the
exact spatial locations of these lower-lying surface states (the $B$ states) and to compare them with the high-bias STM topograph. In order to obtain the energy-resolved real-space mapping of surface states, current imaging tunneling spectroscopy\textsuperscript{12} was performed in this work. Figures 4(b) and 4(c) display a constant-current topographic linescan and a simultaneously acquired conductance plot across the surface dimer rows [the scanning geometry is shown in Fig. 4(a)]. In this measurement, the $B$ states are the dominant surface-state features and the number and spatial locations of the observed topographic maxima are in excellent agreement with the measured conductance maxima. Most strikingly, the energy level of these conductance maxima is in perfect accord with the energy level of the $B$ states measured by averaged normalized conductance spectra. These STS findings clearly establish that the $B$ states are type-I site specific, and therefore originating from the filled surface states of the surface dimer rows, while both type-I and type-II sites, located in the topmost surface bilayer and well resolved in the STM topographs at low sample voltages and small tip-sample separations, are the surface sites of the $A$ states. Also, the existence of two surface states at different energy levels and the faster decay of the $A$ states into the vacuum should be the main factors for observing the bias-voltage dependent imaging phenomenon.

One of the most remarkable features in our proposed structure of the As-terminated AlAs(001)-(3×2) surface. For clarity, only the topmost As layer and the underlying Al layer are sketched. The dangling bonds are shown only for As atoms.
model is the existence of double \( \pi \)-bonded As dimers. It is therefore noteworthy that the observed surface diffusion and resulting 2D nucleus shape, which are strongly affected by the surface dimer configuration, are completely different from the case of MBE-grown GaAs(001)-(2\times4) with a \( \alpha \)-bonded As dimer configuration. The nuclei of AlAs(001)-(3\times2) show a characteristic square shape with major axes along two \{110\} directions.\(^4\) Meanwhile, in the GaAs(001)-(2\times4) case the size of elongated 2D nuclei in the [1\bar{1}0] direction is approximately ten times as much as that in the [110] direction.\(^3\) This can be explained by the highly directional nature of unpaired As dangling bonds on the 2\times4 surface. On the other hand, the observed isotropic behavior in diffusion and nucleation on the surface may be attributed to the delocalized nature of double \( \pi \)-bonded As dimers on the 3\times2 surface. The isotropic step structure with equally smooth [1\bar{1}0] and [110] steps shown in Fig. 1 also supports this argument. Recently, based on their experimental studies on the \( \beta \)-SiC-c(2\times2) surface, Long et al. suggested a structural model involving multiply \( \pi \)-bonded C dimers as the stable surface structure.\(^1\) Interestingly, a large number of Si dangling bonds also exist in their model similar to our case. Although the proposed \( \pi \) structure is supported by our experimental observations, the details regarding how a large number of Al dangling bonds stabilize on the surface are still unclear. Total energy calculations are needed to establish the complete model for the reconstruction and to examine whether the proposed structure is energetically favorable.

In summary, we have performed the first atomic resolution \textit{in situ} STM/STS study of the MBE-grown AlAs(001)-(3\times2) surface and proposed a structural model based on the formation of double \( \pi \)-bonded As dimers and a regular array of missing As-dimer rows on the topmost As-terminated surface. Furthermore, the surface state energies and spatial locations of the AlAs(001)-(3\times2) surface were directly examined by STS. The dramatic differences in the nucleation and growth behavior of (2\times4)- and (3\times2)-reconstructed AlAs(001) surfaces can be primarily attributed to the distinctly different surface and step bond configurations in these two reconstructions.

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