Angle - resolved photoemission study of two phases of the GaAs(100)-c(4x4) surface

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Abstract. We prepared two surface phases of the Ga(001)-c(4x4) reconstruction (α, β) by molecular beam epitaxy (MBE) using As4 and As2 molecular beams and examined the surfaces by angle-resolved ultraviolet photoelectron spectroscopy (UPS) and core level photoelectron spectroscopy with the synchrotron radiation as the excitation source. It is demonstrated that the photoelectron spectroscopy can distinguish between the phases. Appearance of intensive surface state 0.5 eV below the top of the valence band at lower energies is linked to the presence of the β-phases on the surface while in the α-phase spectra the peak is missing. Both As 3d and Ga 3d photoelectron lines show substantial differences between the phases in line shapes as well as in their deconvoluted components. The 3d data are in agreement with different surface composition and atomic structure of both phases.

1. Introduction

The c(4x4) reconstruction on GaAs (001) represents a stable, interesting surface with technological importance. Historically accepted structure of this surface is described by symmetrical three-As dimers model [1] in which the three As dimers per surface unit are bonded to a complete As layer of top GaAs bilayer, giving 0.75 ML As coverage in the topmost layer. (Fig. 1, β-phase ). This model was confirmed by direct STM (Scanning tunneling microscopy) images [2], showing an ordered surface. It was also shown [3], [4], [5] that MBE (Molecular beam epitaxy) preparation conditions and namely the use of either As4 or As2 molecular beams significantly influenced the surface properties. Ohtake et al. [6], [7] reported the existence of the second phase of the c(4x4) reconstruction (denoted as α-phase, next to the traditional β-phase) and proposed its model. The α-phase is described as c(4x4) atomic structure with stoichiometric As/Ga outermost surface composition [6], [7]. In this model the three As dimers in surface unit of the older β-phase are replaced by three As-Ga “mixed dimers” (Fig.1), providing again an ordered STM image [7]. In preparation of the two surfaces the different reactivity of the As beams is utilized. The As2 beam helps in stabilizing the β-c(4x4) surface while the use of As4 beam should produce the α structure only [8]. However, the preparation of the
two phases represents rather a complicated procedure influenced by various growth conditions like As beam chemistry, growth temperature or annealing time [9].

In this paper we aim at preparation of $\alpha$- and $\beta$-phases of the c(4x4) reconstruction and their differentiation by photoemission spectroscopy without having possibility to assign their atomic structure directly.

2. Experiment

The GaAs(001)-c(4x4)-$\alpha$, $\beta$ samples were prepared and characterized by UPS and core level photoelectron spectroscopy at the beamline 41 of the Swedish national synchrotron radiation laboratory MAX-lab in Lund where MBE growth chamber (Kryovak) is attached to the photoelectron spectrometer. This system allows a direct UHV sample transfer between technological and diagnostic parts. Our preparation procedure is based on a phase diagram [8] showing a temperature stability of $\alpha$- and $\beta$-phases in both the As beams. The GaAs : Si substrate ($n=2.10^{17}$ cm$^{-3}$) was first covered by an undoped buffer layer (about 100 nm). Then the (2x4) surface was cooled in either As$_2$ (for the $\beta$ phase) or in As$_4$ (for the $\alpha$ phase) beams to 300°C and annealed for 1 h. After annealing the As cracker cell was shut, the sample cooled to room temperature (in reversed position to prevent As condensation) and immediately transported under UHV to photoemission chamber for a LEED (Low energy electron diffraction) check and photoemission measurements.

3. Results and discussion

3.1. Valence band spectra

Energy dispersed curves of the c(4x4)-$\alpha$ and $\beta$ surfaces are shown in Fig.2. In the $\beta$-phase spectra the surface state 0.5eV below the top of valence band (shaded line) is pronounced in the whole excitation energy region while in the $\alpha$-phase spectra this peak is missing for lower excitation energies. The $\beta$-phase peak represents the surface state from band structure calculations [10] and according to detailed theoretical analysis [11] it is associated with dangling bond on the As dimer in the topmost layer. We expect the As-Ga "mixed dimer" in the $\alpha$-phase to be different enough from the As dimer to suppress the surface state intensity. We therefore take this peak intensity at low excitation energy (e.g. at HeI) for deciding to differentiate between both $\alpha$- and $\beta$-phases.

Remarkable differences in intensity of the 0.5eV surface state were found in earlier studies in the UPS spectra between the c(4x4) surfaces prepared in As$_4$ and As$_2$ beams, the latter having always higher intensity of the surface state under comparable excitation conditions [3], [4], [12], [13]. This supports the mentioned difference between the phases. Chiang et al. [12] did not find the surface state on the surface prepared in As$_4$ beam. That surface could be assigned to the $\alpha$-phase.
3.2 Core level spectra

Ga 3d and As 3d core level spectra are shown in Fig. 3. Both of them, but particularly As 3d profiles, differ distinctly for the two phases and strongly support the diversity of both prepared surfaces. The As peak profile of the \( \alpha \)-phase is similar in shape and deconvoluted components to those in earlier studies of As\(_4\)-grown c(4x4) surfaces [4], [5] (the \( \alpha \)-phase assignment is assisted by the surface composition and indication of Ga dangling bonds reported in [5]). The As\(_2\)-grown surface in [4] is somewhat different from that of the \( \beta \)-phase shown in Fig. 3. One possibility how to understand the contrast is to admit the presence of mixing of the \( \alpha \) and \( \beta \) phases in the data in [4]. According to our data Fig. 3, this mixing should be accompanied by presence of the S\( \text{L} \) component in the As 3d profile which was really reported [4]. (The preparation procedure described in [4], if compared with [8], did not exclude this mixture).

We decomposed the 3d line profiles into minimum number of components needed for reaching the top quality fit. Whereas for the \( \alpha \)-phase three components were necessary, for the \( \beta \)-phase two components were sufficient. Spin-orbital splittings and branching ratio intensity relations used were 0.7 eV and 0.6 for As 3d and 0.44 eV and 0.6 for Ga 3d, respectively. Peak shape was chosen to be a Gaussian-Lorentzian mixture (27%).

Components of the 3d peaks are given in Fig. 3. As and Ga 3d line profiles of the \( \beta \)-phase both represent one bulk and one surface component only while those of \( \alpha \)-phase are more complex, being decomposed into one bulk and two surface components on high (S\( \text{H} \)) and low (S\( \text{L} \)) side of the bulk component position. The S\( \text{H} \) component of the As line profile of the \( \alpha \)-phase is substantially reduced in intensity as compared with its counterpart of the \( \beta \)-phase, reflecting change in the structure composition – one half of the As atoms in the \( \beta \)-phase As dimers is replaced by Ga atoms to form the \( \alpha \)-phase „mixed dimer“. This S\( \text{H} \) component is therefore connected with trigonally bonded surface As. The Ga line profile of the \( \alpha \)-phase has one surface component (S\( \text{H} \)) more than that in the \( \beta \)-phase, so this S\( \text{H} \) component at the \( \alpha \)-
phase is evidently connected with Ga atoms in the topmost „mixed dimer“. A more detailed analysis of 3d lines is not presented here and will be published.

4. Summary

We have prepared α- and β-phases of the c(4x4) surface reconstruction on GaAs(001) and characterized them by photoelectron spectroscopy. The UPS data show that both phases differ in intensity of the surface state 0.5 eV below the top of the valence band. The As and Ga 3d lines in both phases reveal the bulk and surface bonding contributions which again differ in characteristic way. All the data prove the existence of two different c(4x4) surface phases and support their structure and stoichiometry shown in Fig. 1.

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