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Hydrogen adsorption on the GaAs(001)-(2×4) surface: A scanning-tunneling-microscopy study

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Using scanning tunneling microscopy (STM) we have investigated the process of hydrogen adsorption on the GaAs(001)-(2×4) surface. Stepwise hydrogen-induced changes in the atomic structure of the surface are revealed in the STM images. In a first step, one or two hydrogen atoms bond per As atom, giving rise to localized protrusions within the As dimer rows. In a second step, after adsorption of a third H atom per As atom, AsH_3 forms and desorbs, resulting in depressions and thus a degradation of the As dimer rows. Finally, at high exposures a disordered surface develops.

I. INTRODUCTION

The influence of hydrogen adsorption on different reconstructions of the GaAs(001) surface has been studied extensively during the last decades for technological and scientific reasons. For example, the interaction of hydrogen with the GaAs surface is the basis of dry etching methods.[1] Meanwhile, there is strong demand for an understanding on the microscopic scale of the hydrogen adsorption process on the GaAs(001) surface. However, the experimental methods used up to now, such as multiple internal-reflection infrared spectroscopy, high-resolution electron energy-loss spectroscopy (HREELS), reflectance difference spectroscopy (RDS), and spectroscopic ellipsometry,[2–9] do not probe directly the atomic structure. On the (2×4) reconstructed surface As dimers form along [1$\bar{1}$0] on top of a Ga layer.[10–13] Most recent scanning tuneling microsopy (STM) images show the As dimers arranging in blocks of two As dimers followed by two missing dimers forming rows in the [1$\bar{1}$0] direction.[12–14] On this surface the formation of both arsenic and gallium hydrides with hydrogen exposure was found by multiple internal-reflection infrared spectroscopy.[2,3] A model for the hydrogenated surface was proposed with hydrogen breaking the As dimers. The presence of gallium hydrides was attributed to a hydrogen reaction with second-layer Ga atoms. Results of HREELS studies suggest that hydrogen saturates the As dangling bonds at low exposures and thereafter also breaks the As dimer bonds.[4,5] Furthermore, an As loss of the surface with increasing hydrogen exposure, finally resulting in a Ga-rich surface, was found. In agreement with this loss, AsH_3 desorption even at low hydrogen exposures was detected in recent temperature-programmed desorption measurements with a maximum desorption rate at around 330–340 K.[15] No desorption of Ga hydrides was observed.[15] RDS studies attributed the disappearance of characteristic features in the spectral dependence of the surface anisotropy to the removal of As dimers and suggested the onset of surface roughness at high hydrogen exposures.[7–9]

Here we have studied the influence of hydrogen adsorption on the GaAs(001)-(2×4) surface using STM. In contrast to previous work, we are able to analyze directly the atomic structure, providing insight into the hydrogen adsorption process on the microscopic scale. A stepwise hydrogen reaction process is found, where first one or two hydrogen atoms bind to the As atoms or dimers. Thereafter, at higher exposures, the formation and desorption of AsH_3 from the surface results in a degradation of the As dimer rows, leading finally to a disordered (rough) surface.

II. EXPERIMENTAL DETAILS

Si-doped, n-type (1×10^{18} cm^{-3}), homoepitaxial GaAs layers (1 μm thick) were grown on GaAs(001) substrates by molecular-beam epitaxy (MBE) and capped with 50–100-nm-thick As layers deposited from an As_2 cracker cell. After capping, the samples were transferred in air to a UHV chamber equipped with a STM and low-energy electron diffraction (LEED) system. (2×4) reconstructed surfaces were prepared by desorbing the As cap at 350 °C and annealing the surface at 420 °C for 5 min. Further details about the sample preparation can be found elsewhere.[16] It was shown recently that a surface quality similar to one of the as-grown MBE surfaces can be achieved by this procedure.[17] The surface was subsequently exposed to amounts of atomic hydrogen which was produced from molecular hydrogen by dissociation at a hot filament placed about 5 cm away from the sample surface. Hydrogen exposures are given in Langmuir (1 L = 10^{-6} torr molecular hydrogen × 1 s). Note that molecular hydrogen itself does not react with the GaAs surface.[18] Qi *et al.* [3] estimated, using a similar arrangement of the filament with respect to the sample surface and combining mass spectrometry and infrared spectroscopy, the flux of H atoms to the surface to be about 0.1% of the flux of H_2 molecules and the sticking probability of H atoms on the GaAs(001) surface to be between 0.1 and 1.0. After hydrogen exposure the sample

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was transferred to the LEED and STM chambers. LEED patterns and STM images were recorded from the clean and various hydrogen-exposed surfaces. LEED patterns were taken using a four-grid, reverse-view LEED optic. The STM images shown here are constant current topographs with a sample bias of –2.5 V, i.e., probing the occupied electronic states of the surface. The reported bias values refer to the sample voltage with respect to the tip, held at virtual ground.

III. RESULTS AND DISCUSSION

The LEED pattern shows clear (2×4) spots after the above-described sample processing. 100–400-L hydrogen-exposure results first in the disappearance of the 2× LEED spots. After about 1000 L also the ×4 spots disappear and a (1×1) LEED pattern is observed. The same sequence of LEED patterns was previously recorded in conjunction with reflectance difference spectroscopy measurements.[8] STM images obtained from the clean and hydrogen-exposed surface on a scale of 1000 Å ×1000 Å are shown in Fig. 1; those obtained from various hydrogen-exposed surfaces on a scale of 400 Å×400 Å are displayed in Fig. 2. Figure 1(a) shows the clean (2×4) surface with the characteristic As dimer rows in the [1$\bar{1}$0] direction separated by 16 Å. The widely accepted atomic model for this surface superstructure is given in Fig. 3(a).[13,14] The rows are made up of packages of two As dimers followed by two missing dimers. The surface is not atomically flat but exhibits several terraces mostly extending over more than 100 Å×100 Å where the terrace size should be related to the MBE growth conditions of the sample.

Exposure to atomic hydrogen results in a degradation of the surface illustrated in Figs. 2(a)–2(d). After 100 L, hydrogen exposure [Fig. 2(a)] rows which exhibit local contrast variations, i.e., distinct white or dark spots, can be distinguished. Some of these white and dark defects are marked with rectangles and circles, respectively, in Fig. 4, which displays a magnified part of Fig. 2(a). The disappearance of the 2× LEED spots is most likely due to the increased disorder within the rows or could even be a sign for broken As dimers, as will be discussed later. Thus, as a result of the first stage of hydrogen expo-

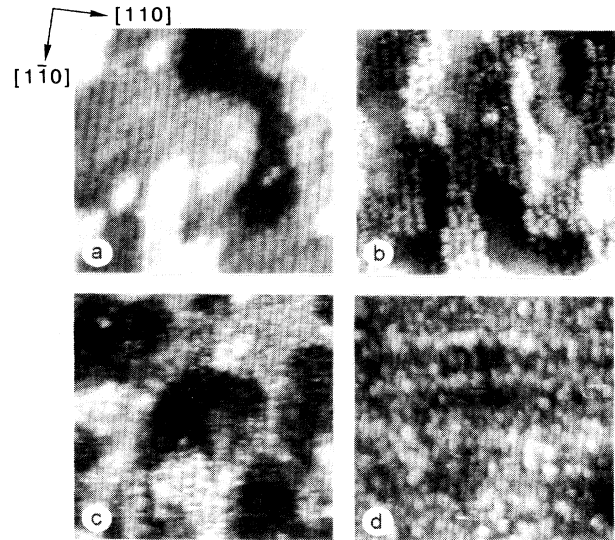

FIG. 2. STM images of the GaAs(001)-(2×4) surface [400 Å×400 Å] after (a) 100 L [LEED: (1×4)], (b) 400 L [LEED: (1×4)], (c) 1000 L [LEED: (1×1)], and (d) 10^5 L [LEED: (1×1)] hydrogen exposure (sample bias: –2.5 V; tunneling current: 0.2 nA). Note that the large white areas correspond to higher terraces.

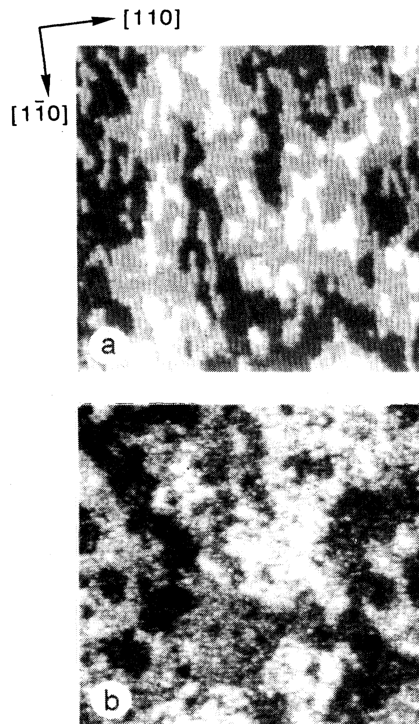

FIG. 1. STM images of the GaAs(001)-(2×4) surface [1000 Å×1000 Å]: (a) clean surface [LEED: (2×4)] and (b) after 10^5 L [LEED: (1×1)] hydrogen exposure (sample bias: –2.5 V; tunneling current: 0.2 nA).

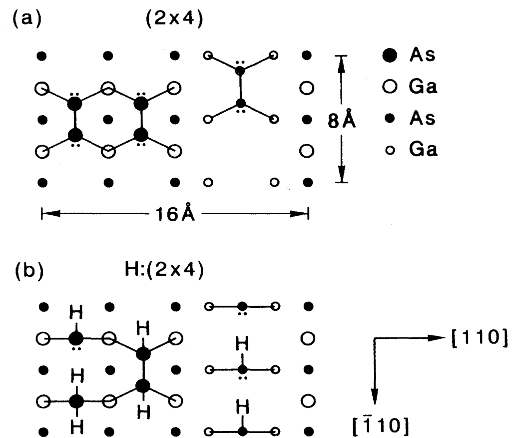

FIG. 3. Atomic model for the clean and hydrogen-terminated surface (taken from Ref. 3).

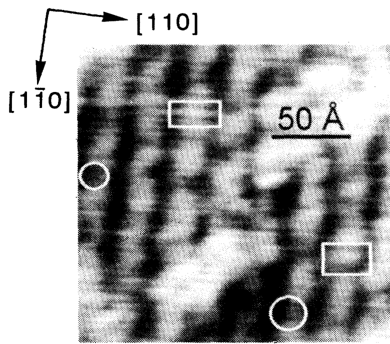

FIG. 4. STM image of the GaAs(001)-(2×4) surface after 100 L hydrogen exposure [magnified part from the upper left of Fig. 2(a) using a different height scale]. Rectangles and circles mark some of the local contrast variations. The white spots (marked with rectangles) are interpreted as hydrogen adsorption sites, the dark spots (marked with circles) as areas where AsH_3 desorbed from the surface. The larger white spots are some defects which could have resulted from the MBE growth or the As decapping procedure.

sure, the dimer rows exhibit pronounced local variations in contrast. Further exposure to atomic hydrogen (400–1000 L) results, as illustrated in Figs. 2(b) and 2(c), in a drastic increase of dark spots within rows and thus disorder. The row structure dissolves, which explains the total disappearance of the ×4 LEED spots at 1000 L. We find a height difference of about 1.4 Å between the dark spots and the rows. Finally, at exposures as high as 10^5 L [Fig. 2(d)] the rows are completely destroyed, i.e., we find a disordered surface, and we observe frequent particle exchanges (most likely As hydrides) between STM tip and surface.

While we monitored so far the influence of hydrogen adsorption on the atomic scale, Fig. 1 now shows the development of the GaAs(001)-(2×4) surface with hydrogen exposure on a larger scale. In this case significant changes take place only for exposures as high as 10^4–10^5 L. After 10^5 L hydrogen exposure [Fig. 1(b)], only the remainders of the terraces are found which are smaller and more irregular in shape compared to the ones found on the clean surface [cf. Fig. 1(a)]. A disordered (rough) surface develops, with corrugations on the 10–20 Å level.

The evolution of the STM images allows us to understand the hydrogen adsorption process on an atomic scale. The hydrogen reaction can clearly be divided into three steps: (I) the appearance of pronounced contrast variations within the As dimer rows, (II) the appearance of depressions within the As-dimer rows, and (III) the creation of a disordered (rough) surface. In the first step (I), one hydrogen atom saturates an As dangling bond. Calculations found an enlarged valence charge density in the vicinity of the As-H bond.[19] We thus interpret the white spots marked with rectangles in the STM image of Fig. 4 as hydrogen adsorption sites. A similar effect of hydrogen adsorption on the valence charge density was oberved in STM studies on the Si(001)-(2×1) surface.[20] Subsequently, a second hydrogen atom will bind to the As atom forming As dihydride, probably by breaking the As dimer according to the model shown in Fig. 3(b) which was proposed by Qi *et al.* in Ref. 3. However, the present STM images do not allow us to distinguish between these monohydrides and dihydrides. At present, we also cannot answer on the basis of the STM images the question of whether and when hydrogen adsorption leads to a breaking of the dimers. However, since the 2× spots in the LEED pattern vanish early, we believe that the dimers do not withstand the H attack for long. In support, RDS measurements showed the removal of As dimers with the adsorption of hydrogen on the GaAs(001)-(2×4) surface and found this process completed after 100 L hydrogen exposure.[8] However, the comparison of the real H exposures is difficult, since a different arrangement of the filament with respect to the sample surface was used there. Hydrogen exposure performed *in situ*, while scanning, is in progress and may allow us to distinguish between these different processes. In the second step (II), attachment of a third hydrogen atom at some As atoms results in the formation of AsH_3 and its desorption. The dark spots within the rows in the STM images after 400–1000 L [Figs. 2(b) and 2(c)] and even after 100 L hydrogen exposure (Fig. 4, marked with circles) indicate such areas where AsH_3 desorbed. The height difference of about 1.4 Å between the dark spots and the rows proves that the Ga layer formerly below the top As layer becomes here the top layer. In agreement, the desorption of AsH_3 was observed at low exposures of 90–300 L in temperature-programmed desorption measurements with a maximal desorption rate at 330–340 K.[15] Also HREELS studies illustrated the As loss of the surface with increasing hydrogen exposure.[4] This process results in the fragmentation of the As row structure. After 1000 L hydrogen exposure, rows are then only faintly indicated [Fig. 2(c)]. The ×4 LEED spots have vanished. The remainder of the rows consist most likely of some leftover of As hydrides. Most of the As dimers are broken in agreement with the *complete* disappearance of the 2× LEED spots. In the third step (III), the exposure to higher amounts of atomic hydrogen results in disorder/surface roughness, with corrugations on the 10–20-Å level. The frequent particle exchanges observed here between STM tip and surface indicates the presence of only weakly bonded surface species. The onset of surface roughness was also suggested from RDS and spectroscopic ellipsometry studies.[7–9] Note that STM clearly demonstrates that etching does not produce deep grooves.

IV. CONCLUSION

We have performed STM measurements in order to elucidate the influence of the adsorption of atomic hydrogen on the (2×4)-reconstructed GaAs(001) surface. The STM images show a stepwise hydrogen adsorption process where first one or two hydrogen atoms bind to the As atoms, resulting in a contrast-rich row structure in the STM images and the disappearance of the 2× LEED spots. Adsorption of a third hydrogen atom at the As atoms results in the formation of AsH_3 and its desorption. Areas where this happened are indicated by holes in

the row structure. At very high exposures, a disordered surface develops with height variations on the 10–20-Å level. At this stage of hydrogen exposure, the surface proves to be very reactive with the STM tip (frequent particle exchanges), i.e., exhibits weakly bound surface species.

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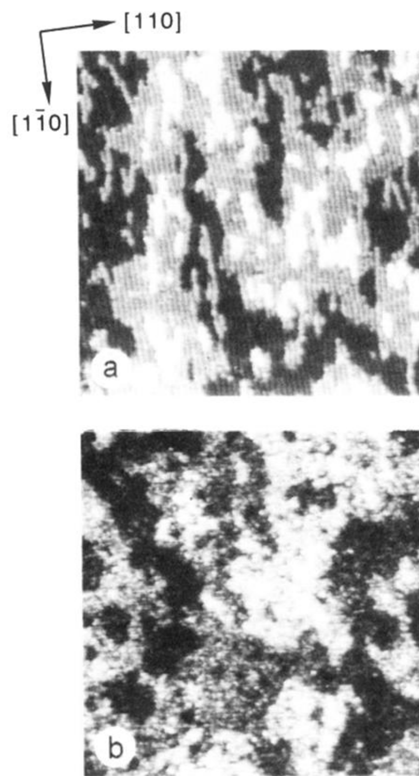

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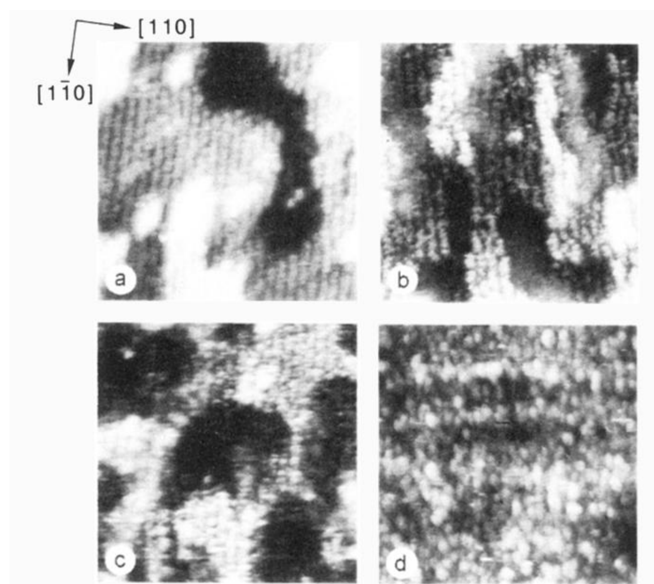

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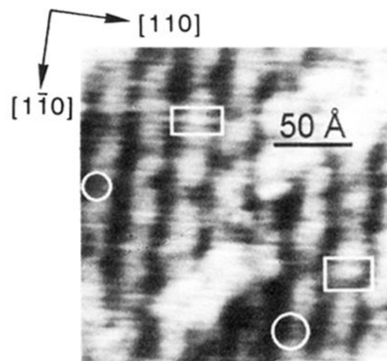

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