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Silicon-induced nanostructure evolution of the GaAs(001) surface

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By using scanning tunneling microscopy and reflection high-energy electron diffraction it is demonstrated that self-organized ordered Si structures develop during submonolayer Si deposition on vicinal GaAs(001) surfaces, provided the preferred adsorption sites in the trenches of the (2×4) reconstruction are filled with Ga. The evolution of different reconstructions with increasing Si coverages is accompanied by step bunching and de-bunching processes. This unexpected behavior is explained by the interaction between reconstructions and steps from a thermodynamic equilibrium view. For particular coverages the complex process leads to a separation of different surface phases and Si coverages on terraces and in step regions.

Understanding the physics of epitaxial growth is a longstanding problem in surface physics and materials science. Of particular interest are the initial stages of growth or the submonolayer regime, which has been extensively studied both experimentally and theoretically for various materials like metals on metals, metals on semiconductors and semiconductors on semiconductors[1–7] with the simplifying assumption that the substrate is immobile during the deposition. The technique of molecular beam epitaxy (MBE) provides an ideal method to study this fundamental issue due to its precision at the atomic level. The investigation of GaAs(001) as a prototype compound semiconductor surface recently revealed that MBE growth may proceed under conditions much closer to equilibrium than has been believed before.[8] From a thermodynamic view, the original substrate surface usually is regarded to be in its equilibrium state.[9–11] Its reconstruction is known to play an important role in step dynamics which determines the morphology of surfaces. Consequently, modification of the surface morphology by deposited atoms is expected to be a common surface phenomenon, as demonstrated, e.g., for Au deposition on vicinal Si(111),[12] restructuring of Cu(110) during oxygen chemisorption[13] and reversible step rearrangements on vicinal Si surfaces as a function of arsenic coverage.[14] However, such possibilities have not yet been explored for III-V semiconductor systems, although such knowledge is important for an understanding of the formation of respective heterogeneous interfaces and self-organized low-dimensional structures. In the present scanning tunneling microscopy (STM) investigation, we show that the ordered incorporation of Si on GaAs (001) surfaces leads to step bunching and debunching processes with increasing coverages. The phenomena are explained in terms of the interplay of the deposited Si and the GaAs template based on thermodynamic arguments.

A number of studies have been devoted to the Si incorporation on GaAs (001) surfaces as they usually are used for Si δ doping and the first step of the Si-on-GaAs heteroepitaxy. In Si adsorption experiments carried out on $c(4\times4)$ reconstructed surfaces,[15] ‘‘needlelike’’ islands were found to form by a Si-As dimer exchange with the additional outermost arsenic layer. Other studies show that Si preferentially occupies the vacant second layer Ga sites in the missing dimer trenches of $(2\times4)\beta$ reconstructed surfaces.[16] It should be noted that steps were not found to influence the Si distribution at above conditions. It is challenging, however, to study the Si incorporation behavior on the $(2\times4)\alpha$ surface which is obtained at higher temperatures or lower As partial pressures. At these conditions the Si atoms have an enhanced mobility and former high-energy electron diffraction (RHEED) and reflectance difference spectroscopy (RDS) studies[17,18] suggested the formation of self-organized structures.

The present experiments were performed in an MBE growth chamber equipped with RHEED and RDS and connected to an STM chamber via a gate valve. Epi-ready *n*-type GaAs substrates with a 2° miscut towards (111)A were used. The structure of the bare GaAs(001) surface after buffer layer growth was closer to the $(2\times4)\alpha$ than the $(2\times4)\beta$ phase at the substrate temperature of 590 °C and an As_4 beam-equivalent pressure of 1.5×10^{-6} Torr, as assessed by RD spectra.[19] Si was deposited with a flux of about 5.0×10^{11} atoms cm^{-2} s^{-1} (calibrated by secondary ion mass spectrometry in reference samples) in pulses of 60 s and interruptions of 180 s. The Si incorporation process which is reflected in the surface structure was monitored by in situ RHEED and RDS. When a certain Si coverage was reached, the deposition was stopped and the resulting surface quenched by decreasing both the substrate temperature and the As_4 background pressure in order to maintain the as-grown surface structures. An unchanged RHEED pattern (judged from real-time linescan measurements) and RDS signal during the whole process were used as criteria for correct quenching. After having the valve of the As_4 source completely closed at a substrate temperature of about 500 °C, the samples were transferred into the STM chamber for further analysis. STM images of filled states were taken at room temperature in the constant current mode with negative sample biases of 2 to 4 V and tunneling currents of 0.1 to 0.4 nA.

During exposure to Si the RHEED pattern of GaAs (001) changes gradually from the $(2\times4)\alpha$ to a (3×2) structure,[20,21] reaching the highest intensity after deposition of 0.3ML (monolayer) Si. Upon further increase of the Si coverage the intensity of the (3×2) surface phase decreases again and a new (1×3) reconstruction,[21] which is related to the so-called asymmetric (1×3) structure of a Si layer with adsorbed As, is formed.

A typical STM image of the clean $(2\times4)\alpha$ surface is shown in Fig. 1(a). The bright and dark rows running in the $[\bar{1}10]$ direction result from the As dimer and missing dimer

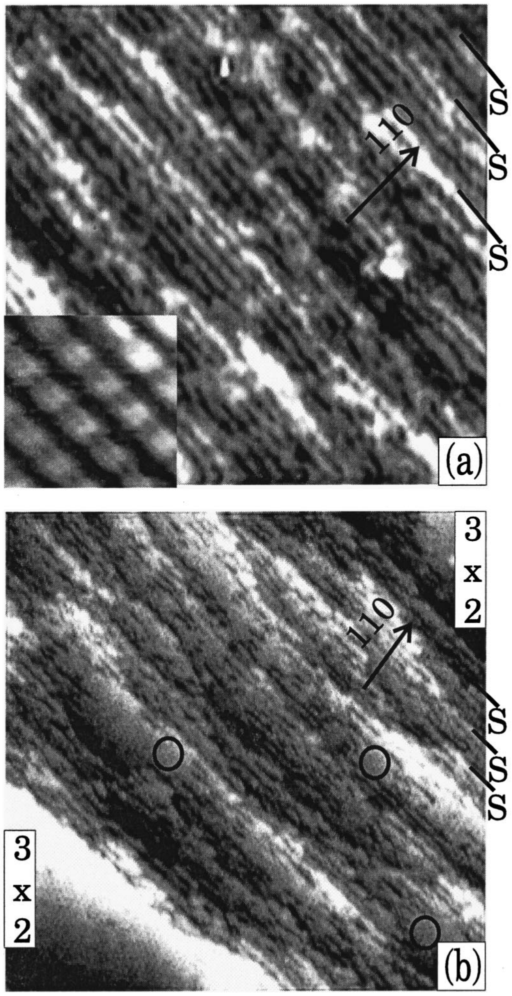

FIG. 1. Filled states STM images of (a) the GaAs(001)-(2 ×4)α surface with a miscut of 2° towards (111)A and (b) the same surface after Si deposition of 0.05 ML. Image dimensions are (a) 60 nm×60 nm and (b) 100 nm×100 nm. Some of the monolayer steps are marked by S. In (b) some of the (3×2) reconstructed patches are indicated by circles. The inset in (a) shows a high-resolution image of the (2×4)β2 structure on the singular surface.

rows, respectively. They are less well resolved than on the (2×4)β surface (shown for comparison in the inset) due to the high kink density in the dimer rows, which is characteristic of the (2×4)α structure.[22] This type of contrast actually can be used as a criterion that the (2×4)α structure was successfully quenched without a transition to the (2×4)β structure. The surface is divided into several terraces by ragged *A*-type monolayer steps (indicated by *S*) roughly running parallel to the dimer rows. The mean terrace width of about 8 nm is consistent with the 2° miscut.

The STM image of Fig. 1(b) was taken after deposition of 0.05 ML Si. Several randomly distributed (3×2) reconstructed patches have formed, with chains spaced 1.2 nm and running along the [110] direction [marked by circles in Fig. 1(b)]. Step bunching and wide (3×2) reconstructed terraces as in the lower left-hand part of the figure are also observed. Upon continuing the Si deposition up to a level of 0.1 ML the Si related (3×2) structure occupies a larger area of the surface at the expense of the original (2×4)α structure [Fig. 2(a)]. The entire surface is covered by wide (3×2) terraces and narrow regions with a heavily distorted (2×4)α structure and step bunching. Fig. 2(b) shows an STM image of the GaAs surface after Si deposition of 0.2 ML. Again, this surface is characterized by large (3×2) reconstructed terraces separated by heavily step-bunched regions. The (2×4)α reconstruction on these terraces is expected to be destabilized, since the terrace width is estimated to be shorter than 1.6 nm.

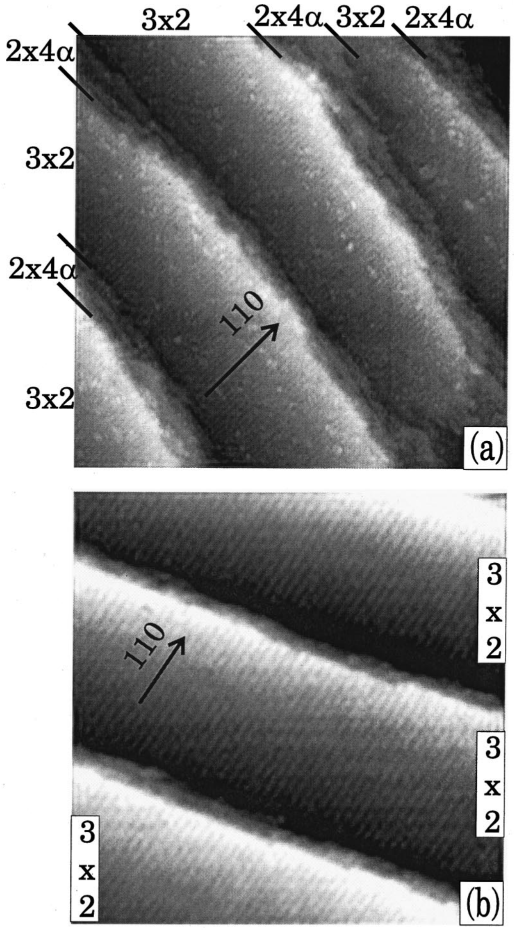

FIG. 2. Filled states STM images of the vicinal GaAs(001) surface after Si deposition of (a) 0.1 ML and (b) 0.2 ML. The image dimensions are (a) 100 nm×100 nm and (b) 60 nm× 60 nm.

From STM image investigation alone the structure of the chains along [110] in the (3×2) reconstruction cannot unambiguously be clarified. By applying RDS and using the difference function between the Si-covered and the bare surface it was shown in previous work[23] that the surface is terminated by Si dimers with the dimer bond along [110]. The STM images of the present work therefore represent the first real space observation of the Si dimer chains and their ordering in ''ribbonlike'' structures on the vicinal surface.

By increasing the Si coverage above 0.3 ML, the surface transforms to the *a*(1×3) structure accompanied by a debunching of the steps. The *a*(1×3) phase is observed only at step regions as shown in Fig. 3(a) for a Si coverage of 0.5 ML. The high resolution STM image in Fig. 3(b) shows that the dimer rows of the *a*(1×3) phase, which run along the [110] direction, have distances of 0.8 nm and 1.2 nm, which gives rise to the incommensurate periodicity along [110]. The RDS analysis reveals that this structure represents a complete Si layer covered by As dimers with dimer bonds along [110].[23] The step debunching processes continue up to

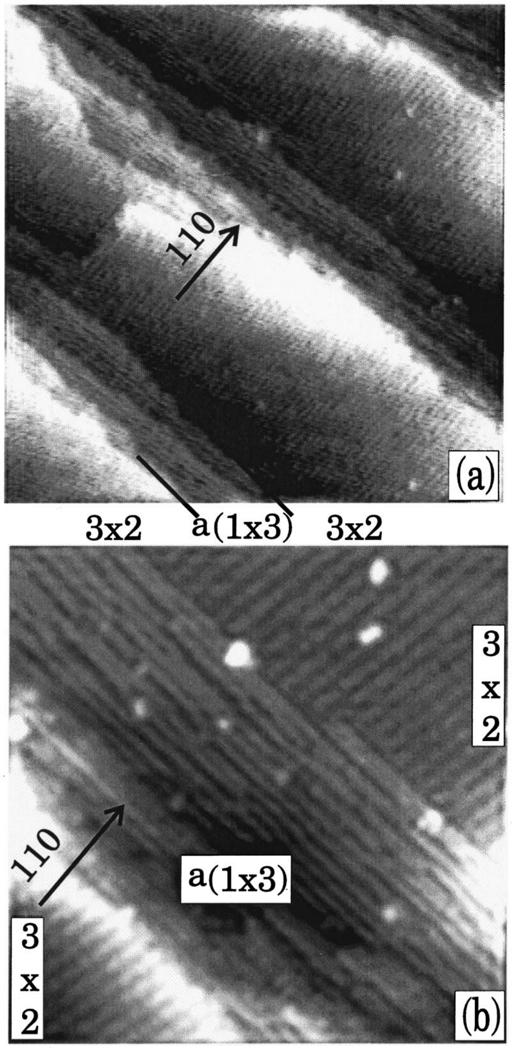

FIG. 3. Filled states STM images of the vicinal GaAs(001) surface after Si deposition of 0.5 ML, (a) 80 nm×80 nm, (b) 32 nm×32 nm.

Si coverages of 0.8 ML where the $a(1\times3)$ reconstruction covers almost the whole surface.

It is important to note that the (3×2) phase is highly ordered except from occasional vacancies, while the $a(1\times3)$ reconstruction is characterized by a disordered appearance. The step bunching phenomenon with the separation into two phases evident from Fig. 3, reveals a distinct self-organized Si structure. Obviously the Si coverage is 1 ML in the step regions and 1/3 ML on the terraces. This unique Si distribution pattern, particularly at low coverages, should be important for electron scattering effects, because of the localized ionized Si atoms which play a dominant role in limiting the carrier mobility at low temperature.

While the (3×2) reconstruction, developing in the early stage of Si deposition, is accompanied by step bunching, the reduction of the (3×2) reconstructed area during the development of the $a(1\times3)$ reconstruction is accompanied by step de-bunching. In view of the growth conditions applied, it is reasonable to discuss this phenomenon in terms of equilibrium thermodynamics.[9,11] The deposited Si atoms induce new reconstructions of the original surface and consequently changes in surface free energy. The excess energy due to the adsorption process must be dissipated. The original structure is no longer an equilibrium state and new equilibration of the surface structure is achieved by surface diffusion. The total terrace energy depends on the coverages of the different surface phases which are determined by the amount of Si deposited. In addition, the reconstruction has implications on the step formation and step interaction energies. It is known that processes such as chemical adsorption and reconstruction change the surface energies by amounts comparable to the small energies of step-step interaction.[11] For the surface equilibration of Si/GaAs(001) we find that the formation of the ordered Si-terminated (3×2) structure, indicative for stronger interaction of surface species, is coupled with step bunching, whereas the formation of the disordered, As-terminated $a(1\times3)$ structure, pointing to weaker interaction of surface species, is coupled with step de-bunching. A more detailed discussion, however, would require knowledge on step formation and interaction energies as well as on the stress.

According to above discussion Si and Ga surface atoms re-distribute due to the interaction between the new Si induced reconstruction and the step structures. Subsequently, the two different coexisting reconstructions with different Si coverages are spatially well separated, which results in an ordered Si incorporation behavior on vicinal GaAs (001) surfaces. To achieve this ordering two requirements has to be fulfilled. The surface diffusion mobility of the Si and Ga atoms must be high and the structure of the initial (2×4) reconstructed GaAs surface must be the α phase. The α phase is characterized by two As-dimers with a complete second Ga-layer and Ga-dimerization.[22,24] Using this template we avoid the empty Ga sites in the missing As dimer trenches of the β-phase that act as favorable Si adsorption sites at low Si coverage.[25] These two prerequisites are the important differences of our present study compared to previous studies by other authors.[15,16]

In summary, self-organized ordered Si structures on the vicinal GaAs (001) surface with well defined adsorption sites were imaged in real space. The results clearly show that the substrate surface of this heteroeptaxial system cannot be considered as immobile. Step bunching and debunching effects occur due to interaction of steps and terrace reconstruction. The unique Si distribution patterns formed are challenges for improving electrical properties by reducing the elastic scattering rate and for future nanotechnology.[25–27]

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[1] G. Rosenfeld, B. Poelsema, and G. Comsa, in *Growth and Properties of Ultrathin Films*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1997), Vol. 8, p. 66, and references therein.

[2] H. Röder, E. Hahn, H. Brune, J.-P. Bucher, and K. Kern, Nature (London) **366**, 141 (1993).

[3] G. Le Lay, in *Growth and Properties of Ultrathin Films* (Ref. 1),

p. 297 and references therein.

[4] Y. W. Mo, B. S. Swartzentruber, R. Kariotis, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **63**, 2393 (1989).

[5] M. C. Bartelt and J. W. Evans, Phys. Rev. B **46**, 12 675 (1992).

[6] V. Bressler-Hill, S. Varma, A. Lorke, B. Z. Nosho, P. M. Petroff, and W. H. Weinberg, Phys. Rev. Lett. **74**, 3209 (1995).

[7] A. R. Avery, H. T. Dobbs, D. M. Holmes, B. A. Joyce, and D. D. Vvedensky, Phys. Rev. Lett. **79**, 3938 (1997).

[8] J. Tersoff, M. D. Johnson, and B. G. Orr, Phys. Rev. Lett. **78**, 282 (1997).

[9] E. D. Williams and N. C. Bartelt, Science **251**, 393 (1991).

[10] E. J. Heller and M. G. Lagally, Appl. Phys. Lett. **60**, 2675 (1992).

[11] E. D. Williams, R. J. Phaneuf, J. Wei, N. C. Bartelt, and T. L. Einstein, Surf. Sci. **294**, 219 (1993).

[12] M. Shibata, I. Sumita, and M. Nakajima, Phys. Rev. B **53**, 3856 (1996).

[13] D. J. Coulman, J. Wintterlin, R. J. Behm, and G. Ertl, Phys. Rev. Lett. **64**, 1761 (1990).

[14] T. R. Ohno and E. D. Williams, J. Vac. Sci. Technol. B **8**, 874 (1990).

[15] A. R. Avery, J. Sudijono, D. M. Holmes, T. S. Jones, and B. A. Joyce, Appl. Phys. Lett. **66**, 3200 (1995).

[16] A. R. Avery, J. Sudijono, T. S. Jones, and B. A. Joyce, Surf. Sci. **340**, 57 (1995).

[17] L. Däweritz, P. Schützendübe, M. Reiche, and K. H. Ploog, Surf. Sci. **385**, L917 (1997).

[18] L. Däweritz, P. Schützendübe, M. Reiche, and K. H. Ploog, J. Vac. Sci. Technol. A **16**, 1969 (1998).

[19] J. Rumberg, J.-T. Zettler, K. Stahrenberg, K. Ploska, W. Richter, L. Däweritz, P. Schützendübe, and M. Wassermeier, Surf. Sci. **337**, 103 (1995).

[20] M. R. Fahy, M. J. Ashwin, J. J. Harris, R. C. Newmann, and B. A. Joyce, Appl. Phys. Lett. **61**, 1805 (1992).

[21] L. Däweritz, K. Stahrenberg, P. Schützendübe, J.-T. Zettler, W. Richter, and K. H. Ploog, J. Cryst. Growth **175/176**, 310 (1997).

[22] T. Hashizume, Q. K. Xue, A. Ichimiya, and T. Sakurai, Phys. Rev. B **51**, 4200 (1995).

[23] L. Däweritz, P. Schützendübe, M. Reiche, and K. H. Ploog, Surf. Sci. **385**, L917 (1997); **402-404**, 257 (1998).

[24] J. E. Northrup and S. Froyen, Phys. Rev. B **50**, 2015 (1994).

[25] K. Shiraishi and T. Ito, Jpn. J. Appl. Phys., Part 2 **37**, L1211 (1998).

[26] R. L. Headrick, L. C. Feldman, and B. E. Weir, in *Delta-Doping of Semiconductors*, edited by E. F. Schubert (Cambridge University Press, Cambridge, 1996), p. 461.

[27] T. Irisawa, J. Motohisa, M. Akabori, and T. Fukui, Jpn. J. Appl. Phys., Part 1 **37**, 1514 (1998).