Confinement of one-dimensional electrons in dimer row segments at Ge/Si(001) surfaces

H. Hirayama*

Department of Materials Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226-8502, Japan

Received 13 January 2004; revised 21 January 2004; accepted 28 January 2004

Available online 12 April 2004

Abstract

During the initial growth, Si(001) surfaces were covered by thin Ge wetting layers. At the wetting layer surfaces, Ge atoms were reconstructed into dimers, which were aligned along the [110] direction to form one-dimensional (1D) ‘dimer rows’. In addition, the dimer rows were partitioned by dimer vacancy lines at the Ge/Si(001) surfaces. As a result, the surfaces were covered spontaneously by an array of 1D dimer row segments. Scanning tunneling microscope images demonstrated that the 1D free-electrons in the dimer rows are confined in each segment and form an ultra-high density array of 1D quantum wells at the surfaces.

Keywords: Ge/Si; Surface; Scanning tunneling microscope; One-dimensional electronic states; Quantum well

1. Introduction

Ge growth proceeds in the Stranski–Klastanov mode on Si(001) surfaces due to the Ge/Si misfit strain [1]. Namely, the Si(001) surfaces are initially covered by two-dimensional (2D) flat Ge wetting layers (Ge coverage \( \theta_{\text{Ge}} < 3 \text{ ML} \)). Three-dimensional (3D) Ge islands then start to nucleate on the wetting layers. The size and density of the Ge 3D islands changes with the Ge coverage, and with suitable growth conditions, the Ge 3D islands are produced in several nanometer sizes. The nanometer size Ge dots could be utilized as quantum dots (QDs) in which electrons are confined. Since the discrete energy levels of the confined electrons can be controlled by their size, the artificial control of the size and spatial position of the QDs has been studied intensively. We utilize the Ge QDs’ tendency to nucleate on locally tensile stressed sites to control the spatial position. The ordered nucleation of the Ge QDs has been demonstrated to be realized by introducing lithographically defined mesa structures [2], or misfit dislocation networks [3] onto the Ge/Si(001) substrate surfaces. The vertical alignment of QDs utilizing the local strain on the apex of the buried QDs has also been reported in the Ge/Si layered structure growth [4].

However, controlling the strain distribution is laborious, and results in a poorly ordered array of QDs. In this paper, we propose an alternative to realizing an ordered array of a quantum confinement system by utilizing the characteristic surface structure of the Ge/Si(001) wetting layer surfaces. In the initial stage of Ge growth on Si(001) substrates, the substrate surfaces were covered by flat, 2D wetting layers. The atoms reconstructed into buckled dimers at the Ge/Si(001) wetting layer surfaces, as well as at Si and Ge(001) clean surfaces [1,5,6]. Fig. 1 shows a typical scanning tunneling microscope (STM) image of the wetting layer surface. At the wetting layer surfaces, the dimers aligned in lines along the [110] direction to construct an array of 1D ‘dimer rows’. The dimer rows in the figure were imaged as chains consisting of bright protrusions (the small white spots) of the dimer atoms. Theoretical studies have indicated that an unoccupied electronic level on the down dimer atoms delocalized fully on the dimer row to become a free-electron like, one-dimensional (1D) empty state (called the \( D_{\text{down}} \) state) at Si and Ge(001) surfaces [7,8]. Since the Ge/Si(001) wetting layer has an electronic structure similar to that of the Si(001) surface [9], the free-electron like \( D_{\text{down}} \) 1D-state is expected to appear on the dimer rows at the Ge/Si(001) wetting layer surfaces. However, the dimer
rows were partitioned by dimer vacancy lines (DVLs), which consist of dimer vacancies aligned perpendicular to dimer rows, at the Ge/Si(001) surfaces. DVLs were imaged as dark lines perpendicular to the dimer rows in the STM image. To minimize the Ge/Si misfit strain, DVLs had nearly equal spacing at the surfaces as shown in Fig. 1 [6,10,11]. Here, we became aware of the possibility that the 1D electrons on the dimer rows could be confined in segments partitioned by DVLs to make up an ultimate high density array of 1D quantum wells (QW) at the Ge/Si(001) surfaces. This paper confirms this idea experimentally using a low-temperature STM.

2. Experiment

Our experimental apparatus has been described in detail elsewhere [6]. In brief, the apparatus consists of ultra-high vacuum (UHV) chambers for the sample and STM tip treatment, STM observation, and Si and Ge molecular beam epitaxial (MBE) growth. The Si(001) surface was cleaned thermally by flashing at 1200 °C in UHV. Ge layers were deposited from a PBN crucible onto the clean Si(001) surface in the MBE chamber. The deposition rate was kept constant (0.056 monolayers (ML)/s), and the Ge coverage was controlled by the deposition time. Ge layers of 0–3 ML were deposited onto the Si substrates at 680 °C. The sample was then cooled to 70 K in the STM chamber with a supercooled liquid nitrogen (Liq. N₂) shroud. The STM images were taken in constant tunneling current mode.

3. Results and discussion

Fig. 2 presents the bias voltage-dependent change of the STM images of 1D dimer rows at Si(001) surfaces. In STM, the spatial distribution of the electron density at an energy equal to the bias voltage is reflected on the images [12]. Since the bias voltage was applied to the sample in our STM, the STM images taken at positive bias voltages represented the spatial distribution of the empty state electrons mainly at the energy equal to the bias voltage measured from the Fermi level. At higher bias voltages ($V_t > +1.5$ V), the protrusions were observed as straight lines running from upper right to lower left. However, the protrusions appeared as zigzag lines at lower voltages ($V_t < +1.4$ V). The energy range with the zigzag protrusions agrees with the energy range of the $D_{\text{down}}$ surface state band. Therefore, the zigzag protrusions are attributed to the characteristic of the spatial distribution of the $D_{\text{down}}$ surface state [13,14]. The dimers were buckled at the Si and Ge(001) surfaces, and the down-end atoms of the buckled dimers aligned alternately in each dimer line to produce zigzag lines topographically [5]. In the buckled dimer, the up-end atom has stereoscopic back-bonds with p-orbital characteristics. Thus, the up-end atom has an s-like dangling...
bond orbital as a counterbalance to maintain sp$^3$ hybridization. In contrast, the down-atom of the dimer has s-like planar back-bonds, and a p-like dangling bond. Therefore, dimer electrons are occupied in the energetically favorable s-like dangling bond on the up-end atoms, and keep the p-like dangling bond on the down atom empty. In the empty state, the p-like dangling bonds on the down-end atoms overlap to construct a 1D conduction band (i.e. $D_{\text{down}}^s$) along the dimer. Therefore, the $D_{\text{down}}^s$ state is expected to have the peaks of its spatial density of state (DOS) distribution on the down-end atoms, resulting in the images of zigzag dimer rows as observed in Fig. 2. At energies above the $D_{\text{down}}^s$ surface conduction state band, a $\sigma^*$ bonding-related surface state exists in the empty state. Since the $\sigma^*$ state has its maximum of the local DOS on the center of the dimer bonds, the protrusions appeared on the straight lines at higher bias voltages as observed in Fig. 2.

At the Ge/Si(001) surfaces, nearly the same bias voltage-dependent changes of the STM images were observed in the empty state at room temperature, though the high-resolution images were more difficult to obtain than at the Si(001) surfaces. The similar bias voltage-dependent change was reasonable, because Ge/Si(001) and Si(001) have nearly the same surface electronic structure [9]. The bias voltage-dependent change suggests that the spatial distribution of the 1D $D_{\text{down}}^s$ state on the dimer chains will be reflected on the STM images taken at $V_t < 1.4$ eV at the Ge/Si(001) wetting layer surfaces.

In the bias voltage range of $V_s < 1.4$ eV, we observed standing wave patterns in the STM images taken at specific bias voltages ($V_{ts}$) at liquid N$_2$ temperature due to the 1D confinement of the $D_{\text{down}}^s$ state electrons in the 1D dimer row segments partitioned between DVLs. An example is depicted in Fig. 3, which is the 3D STM image of the Ge/Si(001) surface taken at $V_s = +1.3$ V at 70 K. The surface Ge coverage was $\theta_{\text{Ge}} = 1.0$ ML. In the figure, the dimer rows extend horizontally, while the dark trench lines extending from the upper to lower sides are DVLs. The length of the dimer row segments was 11 to 12$a_0$ on average ($a_0$ is the 1 $\times$ 1 unit cell length) in this case (namely, for $\theta_{\text{Ge}} = 1.0$ ML). At this surface, the standing wave pattern of $n = 3$ QWS (with three peaks and two nodes) appeared on most of the 1D dimer row segments at $V_s = +1.3$ V.

While decreasing $V_s$ from $+2.0$ to $+1.0$ eV, no standing wave like pattern was observed at $V_s > +1.4$ V at the Ge/Si(001) surface with $\theta_{\text{Ge}} = 1.0$ ML. However, when $V_s$ entered the energy range of the $D_{\text{down}}^s$ surface state band ($V_s < +1.4$ V), the standing wave pattern of $n = 3$ QWS appeared. The $n = 3$ standing wave pattern became most obvious at $V_s = +1.3$ V, and then smeared out. In its place, a new standing wave pattern of the $n = 2$ QWS (with two peaks and one node) appeared on each dimer row segment at $V_s = +1.2$ V. The $n = 2$ standing wave pattern became obvious at $V_s = +1.1$ V, and then smeared out again.

A similar $V_s$ dependence of the STM images was observed at the Ge/Si(001) surface with $\theta_{\text{Ge}} = 1.7$ ML. At this surface, the 1D dimer row segments between DVLs are shorter (8 to 9$a_0$ [6]) than those at the surface with $\theta_{\text{Ge}} = 1.0$ ML. No standing wave pattern was observed at $V_s > +1.4$ V on the shorter dimer segments. In the energy range of the $D_{\text{down}}^s$ surface state band, no $n = 3$ standing wave pattern appeared, and the $n = 2$ standing wave pattern appeared suddenly at a $V_s$ of around $+1.2$ V.

In a 1D QW, QWSs with $n = 1, 2, 3$, etc. have discrete energy levels. Thus, the standing wave patterns with $n$ peaks and $n - 1$ nodes should be observed in STM only at specific $V_s$ that coincide with the discrete QWS energy levels. This expectation agrees with our experimental results. At the Ge/Si(001) surface with $\theta_{\text{Ge}} = 1.0$ ML, the $n = 3$ standing wave appeared at 1.3 eV and $n = 2$ appeared at 1.1 eV, with decreasing $V_s$. This is qualitatively consistent with a QWS with larger $n$ having a higher discrete energy level. Furthermore, the $V_s$-dependence of the Ge/Si(001) surface with $\theta_{\text{Ge}} = 1.7$ ML is reasonably interpreted in the context of the QWS formation on the 1D dimer row segments. Since the QWS energy level increases with the reduction of the well width, $V_s$ corresponding to the $n = 2$ and $n = 3$ standing wave patterns shifted toward the higher energy side at the $\theta_{\text{Ge}} = 1.7$ ML surface with shorter dimer row segments. As a result, the $n = 3$ QWS left the 1D conducting $D_{\text{down}}^s$ surface state band range, and the $V_s$ for $n = 2$ QWS shifted from $+1.3$ V at the $\theta_{\text{Ge}} = 1.0$ ML surface (with a dimer row segment length of 11 to 12$a_0$), to $+1.2$ eV at the $\theta_{\text{Ge}} = 1.7$ ML surface (with a segment length of 8 to 9$a_0$). From these viewpoints, we regard that our STM results
4. Summary

In summary, we examined the possibility of 1D QWS array formation at the Ge/Si(001) wetting layer surfaces. At the surfaces, the 1D dimer rows were partitioned by DVLs with nearly equal spacing. As a result, the surfaces were covered by a densely packed array of the 1D dimer row segments of 0.3 nm in width and 2–3 nm in length. The $n = 2$ and 3 standing wave patterns were observed at specific $V_{ss}$ on each 1D dimer row segment. The $V_s$ and $\theta_{Ge}$ dependences of the appearance of the standing wave patterns indicated that each 1D dimer row segment functioned as a 1D QW. This study demonstrated that an ultra-high density array of 1D QWs was realized at the Ge/Si(001) wetting layer surfaces.

References

[1] B. Voigtlander, Fundamental processes in Si/Si and Ge/Si epitaxy studied by scanning tunneling microscopy during growth, Surf. Sci. Rep 43 (2001) 127–254.
[2] T. Kitajima, B. Liu, S.R. Leone, Two-dimensional periodic alignment of self-assembled Ge islands on patterned Si(001) surfaces, Appl. Phys. Lett. 80 (2002) 497–499.
[3] S.Y. Shiryav, F. Jensen, L.L. Hansen, J.W. Petersen, A.N. Larsen, Nanoscale structuring by misfit dislocations in Si$_{1-x}$Ge$_x$/Si epitaxial systems, Phys. Rev. Lett. (1995) 78503–78506.
[4] E. Mateeva, P. Sutter, J.C. Bean, M.G. Lagally, Mechanism of organization of three-dimensional islands in SiGe/Si multilayers, Appl. Phys. Lett. 71 (1997) 3233–3235.
[5] J.A. Kubby, J.J. Boland, Scanning tunneling microscopy of semiconductor surfaces, Surf. Sci. Rep 26 (1996) 61–204.
[6] H. Hirayama, H. Mizuno, R. Yoshida, Diners at Ge/Si(001) surfaces: Ge coverage dependent quenching, reactivation of flip–flop motion, and interaction with dimer vacancy lines, Phys. Rev. B 51 (2002) 165428(1)–165428(5) and references therein.
[7] A. Ramstad, G. Brocks, P.J. Kelly, Theoretical study of the Si(100) surface reconstruction, Phys. Rev. B 51 (1995) 14504–14523.
[8] M. Rohlfing, P. Kruger, J. Pollmann, Quasiparticle band structures of clean, hydrogen-, and sulfur-terminated Ge(001) surfaces, Phys. Rev. B 54 (1996) 13759–13766.
[9] H.W. Yoem, J.W. Kim, K. Tono, I. Matsuda, T. Ohta, Electronic structure of monolayer and double-layer Ge on Si(001), Phys. Rev. B 67 (2003) 85310(1)–85310(6).
[10] X. Chen, F. Wu, Z. Zhang, M.G. Lagally, Vacancy–vacancy interaction on Ge-covered Si(001), Phys. Rev. Lett. 73 (1994) 850–853.
[11] B. Voigtlander, M. Kasner, Evolution of the strain relaxation in a Ge layer on Si(001) by reconstruction and intermixing, Phys. Rev. B 60 (1999) R5121–R5124.
[12] D. Bonnel (Ed.), Scanning Probe Microscopy and Spectroscopy, Wiley, New York, 2001.
[13] X.R. Quin, M.G. Lagally, View of the empty states of the Si(100)-(2 × 1) surface via scanning tunneling microscopy imaging at very low biases, Phys. Rev. B 59 (1999) 7193–7296.
[14] K. Hata, S. Yasuda, H. Shigekawa, Reinterpretation of the scanning tunneling microscopy images of Si(100)-(2 × 1) dimers, Phys. Rev. B 60 (1999) 8164–8170.
[15] H. Hirayama, R. Yoshida, S. Ishikawa, S. Tanaka, More detailed quantitative analysis and a comparison with calculated wave functions will be published elsewhere. In preparation.