Methods of creating and observing atomically reconstructed vertical Si{100}, {110}, and {111} side-surfaces

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 Appl. Phys. Express 9 085501
(http://iopscience.iop.org/1882-0786/9/8/085501)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 133.1.58.165
This content was downloaded on 01/07/2016 at 08:57

Please note that terms and conditions apply.
Methods of creating and observing atomically reconstructed vertical Si(100), (110), and (111) side-surfaces

Azusa N. Hattori¹,²*, Shohei Takemoto³, Ken Hattori³, Hiroshi Daimon¹, and Hidekazu Tanaka¹*¹
¹Nanoscience and Nanotechnology Center, The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan
²JST-PRESTO, Kawaguchi, Saitama 332-0012, Japan
³Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0101, Japan
*E-mail: a-hattori@sanken.osaka-u.ac.jp; h-tanaka@sanken.osaka-u.ac.jp

We demonstrated the creation of atomically ordered side-surfaces and examined the perfection of the side-surface structures. Atomically reconstructed Si(100), (110), and (111) side-surfaces, which are perpendicular to planar surfaces, were first realized on three-dimensionally patterned Si substrates. The 2 × 1, 16 × 2, and 7 × 7 diffraction spots from the side-surfaces were confirmed by reflection high-energy electron diffraction. Epitaxial ultrathin metal and metal silicide films with an atomically matched lateral interface were grown on the side-surfaces. Methods of creating and observing well-defined surfaces enable the epitaxial growth of an arbitrary geometry, which becomes a key technique for nanoconstruction in three-dimensional space. © 2016 The Japan Society of Applied Physics

Advanced technologies for epitaxial film growth and miniaturization have enabled the continuous development of Si-based devices. Three-dimensionally structured nanometer-size devices, for example, fin field-effect transistors (finFETs),¹¹ have already been produced and commercialized. On such three-dimensional (3D) devices, there are many surfaces with different orientations, not only the general two-dimensional (2D) planar surfaces of polished wafers but also the vertical 3D side-surfaces of fabricated structures. On both 2D and 3D structures, the surface plays an important role in determining the structural and physical properties, because material growth always starts at the surface. However, to date, little attention has been given to controlling the atomic ordering of side-surfaces on 3D structures, and techniques for controlling and investigating 2D surfaces, namely, “surface science” for 2D surfaces, and fabrication techniques for 3D nanoscale structures for 3D integrated circuits⁵ have been individually developed.

On Si nanowire FETs, scattering due to surface roughness severely degrades the mobility.⁵ This means that a perfect surface on a 3D patterned substrate makes it possible to create sophisticated fabrication methods for 3D nanodevices. Some reports have indicated that well-defined side-surfaces can be realized by perfectly alternating the material stacking direction between the out-of-plane and in-plane directions,⁴ leading to improved nanofabrication techniques, especially for growing high-quality nanomaterials⁶ and unveiling the underlying nanoscience.⁵ Atomically ordered 3D substrates with vertical side-surfaces are expected to contribute to not only the expansion of nanostructuring methods but also the development of 3D integrated circuits, which require a vertical connection using electrodes.⁷ To enable atomically ordered nanofabrication on the vertical side-surfaces, a simple and accurate structure evaluation technique is required. Currently, scanning electron microscopy (SEM) is widely used to observe 3D nanoscale structures. However, SEM cannot be used to evaluate structures involving atomic ordering. On the other hand, transmission electron microscopy (TEM) is a powerful technique for examining the atomic structure of 3D nanomaterials, but it is not a convenient one. An alternative method is a diffraction technique. Reflection high-energy electron diffraction (RHEED) enables the examination of surface properties such as the atomic ordering, surface roughness (flatness), and surface homogeneity.⁸ Very recently, Hattori et al. demonstrated the creation of {111}7 × 7 side-surfaces on a Si(110) substrate and showed that an appropriate alignment of the incident electron beam considering the configuration in 3D space enabled RHEED observation of a vertical side-surface.⁴

The arbitrary selection of planes for side-surfaces [Fig. 1(a), inset] can realize higher-performance 3D Si nano-FETs by considering the direction of current flow with higher mobility.⁹ For this purpose, the (100) and (110) planes are suitable for the side-surfaces, in addition to the well-studied (111) plane. In this study, we report the creation of well-ordered Si{100}2 × 1 and {110}16 × 2 reconstructed side-surfaces in addition to a {111}7 × 7 side-surface. By controlling the anisotropic surface reactions in the etching process, the creation of atomically ordered vertical side-surfaces for the primary Si planes was first achieved. RHEED can be used to examine the structures of side-surfaces and confirm the creation of atomically ordered, flat, homogeneous side-surfaces. Moreover, we demonstrate the successful fabrication of an epitaxial ultrathin film on a Si side-surface. RHEED and cross-sectional TEM images showed the formation of a precisely thickness-controlled homogeneous epitaxial film with monolayer (ML) resolution on vertical side-surface planes.

Three-dimensionally patterned Si samples with {100} and {110} side-surfaces, called {100} and {110} samples, respectively, were produced on a commercial mirror-polished Si(100) substrate using a photolithographic technique. Si was etched in an inductively coupled plasma (ICP) reactive ion etching (RIE) system (Samco RIE-400PB). The process parameters were an ICP source power of 300 W, a bias power of 10 W, and a working pressure of 4 Pa. Mixture gases of 10 sccm SF₆, 5 sccm O₂, and 200 sccm Ar were used in the etching cycle, and 40 sccm C₄F₈, 5 sccm O₂, and 200 sccm Ar were used in the passivation process. The parameters in the ICP-RIE recipe were optimized to realize anisotropic Si etching,⁹ which enabled the production of smooth vertical side-surfaces. After dry etching, wet etching was performed to improve the side-surface roughness. In this process, the etching recipe was optimized considering the plane-dependent etching properties.¹⁰ A [100] sample was dipped in 25 wt % tetramethylammonium hydroxide (TMAH) at 70 °C for 3 min. A [110] sample was etched in 25 wt % TMAH with 0.1 vol %...
surfactant (iso-octylphenoxy polyethoxyethanol) at 70 °C for 1 min. After being rinsed with pure water and treated with flowing N₂, the samples were introduced into an ultrahigh-vacuum (UHV) chamber. The samples were degassed and flashed by direct-current heating at ∼1200 °C at a pressure below 2 × 10⁻⁸ Pa. The {100} sample [Fig. 1(b)] has (001) right side and (001) left side-surfaces, and the {110} sample [Fig. 1(c)] has (011) right side and (011) left side-surfaces. SEM images revealed very little deformation of the 3D Si on either of the samples after the flashing procedure. The RHEED patterns were obtained at room temperature (RT) using an electron beam with an energy of 15 keV and a diameter of ~0.5 mm. The direction of the incident electrons is defined by the glancing angle θ and azimuthal angle ϕ for the top and bottom surfaces and the left or right side-surfaces, respectively [Fig. 1(a)]. The intensity of the direct beam (DB) was reduced by a beam stopper. The RHEED patterns were filtered by a computer to emphasize the spot features in the background. Metal and silicide were formed on the side-surface of the three-dimensionally patterned Si with a {111} side-surface ([111] sample). Fe (99.999%) was deposited on the side-surface of a [111] sample at RT using an alumina crucible evaporator. The structure of the Fe-deposited [111] sample was characterized by RHEED, cross-sectional TEM, and high-angular annular dark-field scanning TEM (HAADF-STEM). Details of the preparation of the [111] sample and the RHEED observation are described elsewhere.4) Figures 2(a) and 2(b) show typical filtered RHEED patterns obtained from the {100} sample. The RHEED patterns showed curious characteristics depending on θ, as shown in Figs. 2(a) and 2(b). The DB position did not change during the RHEED observation. Figure 2(a) (θ = +0.4° and ϕ = −1.2°) shows two overlapping Si[100]2 × 1 reconstructed diffraction patterns8,11) that originated from the top/bottom and left side-surfaces. One is a semicircular (100)2 × 1 pattern having a shadow edge SE(100) in the horizontal direction. The other is a (001)2 × 1 pattern on the left quarter-side with a shadow edge SE(001) in the vertical direction. We can see that the diffraction spots on the left side are slightly elongated in the horizontal direction, which is characteristic of a RHEED pattern from a side-surface.4) The diffractions from the top and bottom surfaces disappeared and those from the left side-surface remained when we changed θ from +0.4° to 0.0°. In Fig. 2(b) (θ = 0.0° and ϕ = −1.2°), only a quarter-circle 2 × 1 pattern with strong Kikuchi lines and bands appears, corresponding to the relationship between θ and ϕ, that is, the glancing and azimuth angles for each surface.4,8) Quarter-circle 2 × 1 patterns were also observed on the right when ϕ
was positive. The left side of Fig. 2(c) shows the reciprocal lattice of the Si{100}2 × 1 reconstruction, corresponding to the left side and top/bottom surfaces of the {100} sample. The 2D reciprocal lattice of Si(001) is perpendicular to that of Si(100), and the common crystalline direction is $\frac{1}{2}00/C_{2210}\parallel C_{138}$. The Ewald constructions on the (100) top and bottom and (001) left side-surfaces in the 3D reciprocal space in our experimental setup, namely, the simulated RHEED patterns at $\theta = +0.4^\circ$ and $\phi = -1.2^\circ$ [Fig. 2(c), right panel] show good agreement with the observed RHEED pattern [Fig. 2(a)]. These results indicate that atomically flat side-surfaces were achieved on the {100} sample.

The creation of atomically ordered {110}16 × 2 side surfaces was also realized. Figure 3(a) shows the RHEED patterns from a {110} sample observed at $\theta = +0.4^\circ$ and $\phi = +1.1^\circ$ with eye-guides for $\langle 1/C_{2210} \rangle$ and (100). Inset shows the relationship between the incident beam and the surfaces schematically. Schematics of 2D reciprocal lattices on (b) Si(100)2 × 1 (left panel) and (c) Si(001)16 × 2, corresponding to the top/bottom and right side-surfaces, respectively, on the {110} sample as shown in (d).

Fig. 3. (a) RHEED patterns from the {110} sample observed at $\theta = +0.4^\circ$ and $\phi = +1.1^\circ$ with eye-guides for (110) and (100). Inset shows the relationship between the incident beam and the surfaces schematically. Schematics of 2D reciprocal lattices on (b) Si(100)2 × 1 (left panel) and (c) Si(001)16 × 2, corresponding to the top/bottom and right side-surfaces, respectively, on the {110} sample as shown in (d).

Atomically well-defined side-surfaces on a substrate can make an enormous contribution to nanofabrication. To demonstrate the applicability of material growth on such side-surfaces with atomic resolution, we produced Si{111}–Fe side-surface structures and investigated them using TEM. Figures 4(a)–4(d) show cross-sectional TEM and HAADF-STEM images of a 0.4-nm-thick Fe layer deposited on the {111} right side-surface of the {111} sample. We can see four and five MLs of $\alpha$-Fe on the {111} right side-surface, where a smooth in-plane heteroepitaxial interface with a length of 50 nm or more was formed between $\alpha$-Fe and Si. The relative orientations of the $\alpha$-Fe and the Si right side-surface are $\langle 110 \rangle_{\text{Fe}} \parallel \langle 111 \rangle_{\text{Si}}$ and $\langle 112 \rangle_{\text{Fe}} \parallel \langle 112 \rangle_{\text{Si}}$, which are similar to those in previous reports on Fe on a 2D Si(111) surface. Ag was also deposited on the {111} left side-surface. A cross-sectional TEM image (not shown) showed...
that face-centered cubic Ag grew epitaxially with an atomically matched interface, Ag\((\{111\}/\text{Si}\{111\})\), without any visible defects or dislocations. Our results clearly show that a coherently grown (ultra)thin film was realized on the vertical side-surface and that the growth alternated between the out-of-plane and in-plane directions. Of course, the silicidation reaction can be controlled on the side-surfaces. Figure 4(d) shows a typical RHEED pattern for a 0.4-nm-Fe-deposited Si\(_3\) reaction can be controlled on the side-surfaces. We can confirm 2 \times 2 (streaky) spots (orange arrows) showing the formation of c-FeSi.\(^{10}\) Simultaneously, Si\((\{111\})\sqrt{3} \times \sqrt{3}-\text{Ag}\)\(^{8,11,13}\) was obtained on the left side-surface. These results show that highly developed thin-film formation techniques are applicable for the vertical side-surface of three-dimensionally patterned substrates, and the material stacking direction can be perfectly switched between the out-of-plane and in-plane directions. Thus, we can conclude that it is possible to fabricate high-quality nanomaterials on three-dimensionally patterned Si while obtaining the advantages of design in an arbitrary 3D space. In this study, we prepared a side-surface with a height of \(\sim 10\)\(\mu\)m and a length of 20–100\(\mu\)m to obtain intense RHEED intensity from the side-surfaces. We can reduce the height and length to \(\sim 10\) and \(\sim 30\)\(\mathrm{nm}\), respectively.\(^9\) The adjustability of the side-surface size can provide new possibilities for realizing novel size-induced surface phenomena.

In summary, we successfully created \{100\}\(2 \times 1\), \{110\}\(16 \times 2\), and \{111\}\(7 \times 7\) vertical reconstructed side-surfaces on three-dimensionally patterned Si substrates. The surfaces were evaluated in 3D space using RHEED, which has been used previously only for 2D planar substrates. Producing vertical and flat side-surfaces requires an optimized dry-etching recipe and suitable wet-etching for each plane considering the anisotropic etching reaction. Flashing in UHV as the final step produces clean reconstructed side-surfaces. The formation of ultrathin Fe, Fe silicide, and Ag layers on side-surfaces was demonstrated. These results show that epitaxial growth with an arbitrary geometry in 3D space is possible, allowing the transfer of well-developed surface- and interface-controlling techniques on 2D Si surfaces. An atomically matched vertical interface between a metal and a semiconductor does not degrade the device performance and has high potential for the use of integrated materials. Our approach in this study will contribute to the realization of high-performance 3D nanoscale integrated devices.

**Acknowledgments** The authors are grateful to Kazumi Konda, Michiko Sakuma, and Takeshi Ishibashi for their helpful assistance. The authors also thank the staff of the Comprehensive Analysis Center (ISIR, Osaka University). Part of this work was also supported by the “Nanotechnology Platform Project (Nanotechnology Open Facilities in Osaka University)” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (F-15-OS-0005).

---

13. The reconstructed surface unit vectors from Si\((\{110\}/\text{2} \times \text{1}\)) are defined as \(a_{110}^s = \frac{1}{a} a_{10}^s\) and \(h_{110}^s = \frac{1}{a} h_{10}^s + \frac{1}{c} h_{10}^s\) (domain A, purple points) and \(a_{110}^s = \frac{1}{a} a_{10}^s\) and \(h_{110}^s = \frac{1}{c} h_{10}^s\) (domain B, green points), as shown in Fig. 3(a). In Fig. 3(a), domain A is considered only for the (110) eye-guide.