Creation of atomically flat Si\{111\}7 × 7 side-surfaces on a three-dimensionally-architected Si(110) substrate

Azusa N. Hattori \textsuperscript{a,*}, Ken Hattori \textsuperscript{b}, Shohei Takemoto \textsuperscript{b}, Hiroshi Daimon \textsuperscript{b}, Hidekazu Tanaka \textsuperscript{a}

\textsuperscript{a} Nanoscience and Nanotechnology Center, The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihoga-oka, Ibaraki, Osaka 567-0047, Japan

\textsuperscript{b} Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama 8916-5, Ikoma, Nara 630-0192, Japan

\textsuperscript{*} Corresponding author.
E-mail addresses: a-hattori@sanken.osaka-u.ac.jp (A.N. Hattori), h-tanaka@sanken.osaka-u.ac.jp (H. Tanaka).

\textbf{A R T I C L E I N F O}

Article history:
Received 27 July 2015
Accepted 4 September 2015
Available online 11 September 2015

Keywords:
Si\{111\}7 × 7
Three-dimensional (3D)
Side-surface
Reflection high-energy electron diffraction (RHEED)

\textbf{A B S T R A C T}

The realization of atomically flat side-surfaces, which are vertical planes on a substrate, would make an enormous contribution to a paradigm shift from two-dimensional planar film structures to three-dimensional (3D) nanostructures. In this paper, we demonstrate the successful creation of well-defined Si\{111\}7 × 7 side-surfaces on a 3D-architected Si(110) substrate by the combination of 3D Si patterning and surface preparation techniques, as confirmed by reflection high-energy electron diffraction (RHEED). The RHEED patterns consisted of 7 × 7 diffraction spots from the Si\{111\} side-surfaces and 2 × 16 diffraction spots from the Si(110) top/bottom surface. We also performed the deposition of metals (Au and Ag) onto the side-surfaces, leading to the formation of Si\{111\} v3 × v3R30°-Au and Si\{111\} v3 × v3R30°-Ag structures. This is the first demonstration indicating super-reconstructions of such well-defined side-surfaces.

© 2015 Elsevier B.V. All rights reserved.

\section{1. Introduction}

The significance of nanostructuring techniques has increased with the progress of scaling down devices to a nanometer order. The realization of three-dimensionally (3D)-architected nanostructures, i.e., the transformation from novel two dimensional (2D) film-based devices to 3D nanodevices, is of crucial importance to future electronic applications \cite{1}. So far, various nanofabrication techniques have been proposed and developed with different levels of success. In many cases, materials grown on the substrates are affected by the substrate structure such as the shape, roughness, dimensionality, and so on. 3D-patterned substrates prepared by the conventional lithographic method can be used to form 3D nanostructures. Although considerable attention has been devoted to controlling the size, shape, and positioning in research on patterning, little attention has been focused on the atomic ordering of the surfaces on 3D-patterned substrates. The realization of perfect surfaces on 3D structures may be a requirement to produce high-quality samples. Since material growth starts on the surface, the surface condition clearly determines the structural and physical properties of the grown materials. Recently, there have been reports on 3D nanostructuring considering the surface condition on 3D-patterned substrates, namely the side-surfaces \cite{2-5}, where functional metal-oxide nanowire structures were successfully fabricated on the side-surfaces of 3D crystalline substrates. These results strongly indicate that the atomically well-defined side-surfaces on a substrate would make an enormous contribution to the fabrication of well-ordered 3D nanostructures, leading development to the new research field and fulfilling urgent industrial requirements.

In this study, we demonstrate a 3D-architected Si(110) substrate with atomically-ordered side-surfaces having a 7 × 7 reconstruction. An original strategy for the realization of the atomically flat side-surfaces is to combine 3D-patterning and surface science based techniques for Si. The isotropic plasma etching of Si \cite{6} was employed to obtain a 3D-patterned structure on a Si(110) substrate. Considering the crystallographic geometry, i.e., the plane orientations (Fig. 1(a)) and the surface stability, Si(110) was figured to produce vertical \{111\} side-surfaces. Optimized treatments of wet etching and annealing in ultra high vacuum (UHV) enabled us to obtain atomically ordered Si surfaces on the fabricated wall surfaces. Notably, the reflection high-energy electron diffraction (RHEED) from the \{111\} side-surfaces, which are perpendicular to the substrate (110) plane, indicated a 7 × 7 reconstructed structure. We also demonstrated side-surface reconstructions induced by separate depositions of metals, i.e., side-surface structures of Si(111)v3 × v3R30°-Ag right-side and Si(111)v3 × √3 × 3R30°-Au left-side surface. The successful formation of reconstructed structures on side-surfaces illustrates the application potential of such the side-surfaces in improving the nanostructuring techniques, especially for growing high-quality nanomaterials and unveiling the underlying nanoscience.
2. Experimental procedure

The 3D-architected structures were produced on a commercial mirror polished Si(110) substrate (Sb-doped, 1–10 Ω cm) using a photolithographic technique. A line (20 μm width and 2 mm length) mask pattern was drawn using g-Line positive photoresist (OPFR-5000, TOKYO OHKA KOGYO). Si was etched in an inductive coupled plasma (ICP)-reactive ion etching system (RIE-400iPB, Samco). 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. As shown in Figs. 1(b)–1(d), the lines lied parallel to [112] direction. The etched Si depth, i.e., the height of the Si lines, was about 10 μm. The area of the 3D-patterned Si on the Si(110) substrate (3 × 26 × 0.3 mm³) was 2 × 15 mm² (Fig. 1(b)). Note that the outer-shape of the substrate reflects [111] cleaved planes. After the removal of the photoresist mask by acetone, the 3D-patterned Si(110) substrate (3D-Si) was dipped in a Si etchant (Pure Etch 160, Hayashi Pure Chemical Ind.) for 3 min, rinsed with pure water, dried by blowing with N2, and introduced into the UHV chamber.

The 3D-Si substrate was degassed and flashed by direct-current heating at –1150 °C at a pressure below 2 × 10⁻⁸ Pa. Deformation of the 3D-Si was hardly observed after the flashing in scanning electron microscopy (SEM), that is, the vertical [111] walls were maintained. Au (99.99%) and Ag (99.99%) were deposited on the 3D-Si at room temperature (RT) using an alumina crucible evaporator. The Au and Ag thicknesses were ~0.2 nm and ~1.0 nm, respectively, estimated by a thickness monitor. The Au deposition angle from [110] to [TT] (Fig. 1(d)) was set to ~80°, corresponding to the deposition on the left wall deposition. Similarly, the Ag deposition angle from [110] to [TT] was ~80° for the right wall. Au and Ag were slightly deposited on the top (110) surfaces. Subsequently, the sample was annealed at 500 °C, typically for 10 min. RHEED patterns were obtained at RT using an electron beam with 15 keV in energy and ~0.5 mm in diameter. The direction of the incident electrons is defined by the glancing angle θ and azimuthal angle ϕ for the top and bottom Si(110) surfaces (Fig. 2). θ was changed from −0.6° to +1.4°, ϕ, which is defined from the angle to [112] in the in-plane direction, was changed from −4.5° to +4.7°. The RHEED patterns were filtered by a computer to emphasize the spot features in the background.

3. Results and discussion

Figure 3 shows typical filtered RHEED patterns obtained from 3D-Si(110) at various θ and ϕ. The RHEED patterns showed curious characteristics, because the half of patterns were removed, that have not been reported to the best of our knowledge. We notice that the diffraction spots on the left side (Fig. 3(a)) and the right side (Figs. 3(b) and 3(c)) elongate a little in the horizontal direction. In general, the elongate (streaky) direction corresponds to surface normal direction [7], as illustrated in Fig. 2. Thus, these little streaky spots indicate the existence of vertical side-surfaces.

In Figs. 3(a) (θ = +0.3° and ϕ = −1.6°) and 3(b) (θ = +0.3° and ϕ = +1.1°), diffraction spots from the direct beam (DB) can be observed in the 1/7 th-order Laue zones (112, 112, 112) in the left and right quarter-sides, respectively, as well as seven spots within the Kikuchi-band width (e.g., indicated by a pink arrow in Fig. 3(a)). These patterns clearly correspond to Si(111)7 × 7 reconstruction [7], having shadow edges in the horizontal and vertical directions. Fig. 3(a) (3(b)) corresponds to Si(111) (Si(111)) 7 × 7 diffraction on the surface of the left-side (right-side) wall of the 3D-patterned structure. Note that a specular spot (00) (111), (00) (111) from the DB appears on the left (right) side. In addition, strong Kikuchi lines and bands were observed in the side RHEED pattern. These results indicate that atomically flat side-surfaces were achieved on the 3D-patterned Si(110) by etching and UHV annealing. We consider that the plasma and chemical etching conditions were affectively optimized to fabricate a nearly vertical wall structure and produce the stable Si(111) crystal planes, respectively. Finally, UHV flashing resulted in clean reconstructed side-surfaces while maintaining the vertical wall structures.

In Figs. 3(a) and 3(b), spots in the half Laue zone (112) can be seen on both right and left sides, though the spots are weak at the sides over-lapping with the 7 × 7 patterns. The 112 spots correspond to a clean Si(110) surface with 2 × 16 reconstructions [8,9]. Figure 4(a) shows the two-dimensional reciprocal lattice of Si(110); the top and bottom surfaces of the 3D-patterned structure are shown in Fig. 4(c). The Si(110) 2 × 16 reconstruction has two domains; domain A produces a...
circle of spots in L1/2, as shown in the simulated RHEED pattern at nearly the \( \frac{1}{2} \) incidence in Fig. 4(d). The weak streaky spots in Figs. 3(a) and 3(b), some of which are indicated by green arrows in Fig. 3(a), can be assigned to domain B (Fig. 4(a)). Kikuchi lines from Si(110) are also seen in the 7 × 7-absent region. The existence of the 2 × 16 pattern and Kikuchi lines shows that flat Si(110) areas at the top and/or bottom surfaces with the 2 × 16 reconstructed double domains are also produced by the chemical etching and UHV flashing.

Part of Fig. 4(b) shows the reciprocal lattice of Si(111) 7 × 7 reconstruction, corresponding to the right side surface of the 3D-Si wall (Fig. 4(c)). Note that the two-dimensional reciprocal lattice of Si(11T) (Fig. 4(b)) is perpendicular to that of Si(110) (Fig. 4(a)), both of which have the common crystalline direction of [1T2]. This leads to the 7 × 7 spots in the right side of the simulated RHEED pattern (Fig. 4(d)). For instance, the cross section of the (T1) rod (Fig. 4(b)) with the Ewald sphere \([7]\) is the (T1) \((111)\) spot on the right side in a simulation, as observed in Fig. 3(b). Fig. 4(d) also shows that the L_0 (L_1) arc of Si(1TT) is the same as that of Si(110), as expected from Figs. 4(a) and 4(b). The Ewald constructions on the (110) top/bottom and (11T) right-side surfaces in a 3D reciprocal space satisfactorily reproduce the unprecedentedly observed RHEED pattern.

The appearance of the left-side and right-side Si(111)7 × 7 patterns depends on \( \phi \), as seen in Figs. 3(a) and 3(b). \( \phi \) is the azimuth angle for the Si(110) top/bottom-surfaces and simultaneously corresponds to the glancing angle for the Si(111) side-surfaces. On the other hand, \( \theta \) is the glancing angle for Si(110) and also acts as the azimuth angle for Si(111). Table 1 summarizes the relationship between \( \theta \) and \( \phi \) and the glancing and azimuth angles for the surfaces. This table also shows the observable and non-observable conditions in the RHEED patterns depending on the polarity of \( \theta \) and \( \phi \). When \( \theta \) (the glancing angle for

### Table 1

<table>
<thead>
<tr>
<th>Top/bottom surface</th>
<th>Side surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>Right (T1)</td>
</tr>
<tr>
<td>Glancing angle</td>
<td>Azimuth angle</td>
</tr>
<tr>
<td>( \theta )</td>
<td>( \phi )</td>
</tr>
<tr>
<td>+</td>
<td>○</td>
</tr>
<tr>
<td>-</td>
<td>×</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Azimuth angle</th>
<th>Glancing angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>○</td>
</tr>
<tr>
<td>+</td>
<td>○</td>
</tr>
<tr>
<td>-</td>
<td>×</td>
</tr>
</tbody>
</table>

The intensity of the direct beam (DB) was reduced by a beam stopper. The insets schematically show the relationship between the incident electron beam and the 3D-Si, indicating the observable surfaces.
Si(110) decreases, the RHEED pattern from Si(110) disappears, while a pattern from Si(111) is present. Indeed, in Fig. 3(c) (θ = 0° and φ = +1.9°), a quarter-circle 7 × 7 pattern is seen with faint 2 × 16 spots. One can see the characteristic φ- and θ-dependences of the RHEED patterns in Figs. S1 and S2 (Supporting Information), respectively. These RHEED patterns clearly show that all the surfaces on the 3D-Si, i.e., the (110) top/bottom surfaces, the (110) right-side surface, and the (111) left-side surface, have atomically ordered structures.

To demonstrate the applicability of material growth onto such side-surfaces, we produced Si(111)-Au, and -Ag reconstructed side-surface structures. Au and Ag were deposited on the (111) left-side and (111) right-side surfaces, respectively, and the sample was subsequently annealed. Fig. 5(a) and 5(b) show typical RHEED patterns obtained from the left-side and right-side surfaces, respectively. We can confirm $\sqrt{3} \times \sqrt{3}$ (streaky) spots in $L_0$ (orange arrows) in both Figs. 5(a) and 5(b), which correspond to the $\sqrt{3} \times \sqrt{3}$ rods in Fig. 4(b). The spots in $L_1$ were faint under the observed conditions in Fig. 5(a) but visible in Fig. 5(b) (green arrows). The RHEED patterns indicate the formation of Si(111)$\sqrt{3} \times \sqrt{3}$-Au [7,9,10] and Si(111)$\sqrt{3} \times \sqrt{3}$-Ag [7,9,10], namely, different materials are able to be independently grown on each side surface.

Thus, our results demonstrate the potential for realizing complex 3D nanostructures, such as in-plane multiple heterostructures, with atomically ordered surface structures.

4. Summary

We have successfully formed a 3D-architected Si structure on a Si(110) substrate having Si(110)$2 \times 16$ at the top and/or bottom surface and Si(111)$\sqrt{3} \times \sqrt{3}$-Au, and $\sqrt{3} \times \sqrt{3}$-Ag at the side surfaces. To our knowledge, this is the first report of the RHEED patterns of super-reconstructions from such well-defined side-surfaces. The demonstrations reported in this paper indicate that method of manufacturing and evaluating surfaces can be developed from current two-dimensional space to three-dimensional space. It is noteworthy that RHEED is a valid technique for investigating the 3D structures. The approaches used in the present research are expected to contribute to the realization of well-ordered 3D nanofabrication, where the material stacking direction can be perfectly switched between the out-of-plane and in-plane directions. Novel 3D nanostructures are also expected to help unveil the underlying 3D surface science phenomena.
Acknowledgments

The authors appreciate Kazumi Konda, Michiko Sakuma, and Shoichi Sakakihara 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 “Nanotechnology Platform Project (Nanotechnology Open Facilities in Osaka University)” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan [Nos. S-15-OS-0012 and F-15-OS-0013], and The Murata Science Foundation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2015.09.002.

Fig. 5. Typical RHEED patterns obtained from of (a) Si (111) left-side surface (θ = +0.1° and φ = −2.6°) deposited with Au and (b) Si (111) right-side surface (θ = +0.1° and φ = +2.2°) deposited with Ag. Spots in the L₃ Laue zone indicating by orange arrows correspond to the √3 × √3 the reciprocal-lattice rods in Fig. 4(b).

References