Three-Dimensional Reciprocal-Lattice Analysis Using Azimuth-Scan Reflection
High-Energy Electron Diffraction: Determination of Complex Crystal Orientations of Al Grains on Si(111) Surface

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We have applied a three-dimensional (3D) reciprocal-lattice analysis method using a typical reflection high-energy electron diffraction (RHEED) system — all RHEED patterns in scanning sample-surface azimuth are converted into 3D reciprocal-lattice space. This analysis method can determine complex crystal orientations of nanoclusters, islands, and grains with multiple domains, which are difficult to obtain from a small number of non-converted two-dimensional RHEED patterns. For an Al-deposited Si(111) surface followed by annealing, we successfully determined new crystal orientations of Al grains: Al(001), Al(012) and Al(011) || Si(111) with Al[010] || Si[011]. The typical acquisition time of 3D RHEED patterns is 10–20 min, which is shorter than that by a standard X-ray diffraction system with φ and ω scans for 3D reciprocal-lattice mapping. This is one of the advantages of this analysis method, in addition to the convenient observation of in situ vacuum-fabricated nanocrystals on substrate surfaces with high sensitivity.

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1. Introduction

The transmission electron diffraction patterns obtained by transmission electron microscopy (TEM) and reflection high-energy electron diffraction (RHEED) are useful for identifying the crystal structures and orientations of nanoclusters, islands, and grains fabricated on substrates. In simple cases, we can often identify them from a few diffraction patterns. For instance, in the case of nanocrystals with a single domain, a diffraction pattern at the incidence of an electron beam along a highly symmetric orientation shows well-arranged transmission spots, which can be analyzed easily. For complex cases, however, the analysis of the structures and orientations is difficult at a glance from a few diffraction patterns, owing to multiple domains with unexpected orientations, streaks from nanocrystal facets, lack of diffraction spots depending on the nanocrystal shape, and so on. To understand the overall crystalline feature of structures, it is useful to map a three-dimensional (3D) reciprocal lattice converted from multiple diffraction patterns with various incident angles of an electron beam.

Figure 1 shows a schematic diagram of creating a 3D reciprocal-lattice map from transmission diffraction patterns when a nanocrystal on a substrate is rotated around the normal direction of the substrate surface (azimuth, φ-scan). Since the 3D reciprocal-lattice points of the nanocrystal crossing with the Ewald sphere of the incident electron beam are projected as transmission diffraction spots on the screen, the obtained diffraction spots as a function of the φ angle can be converted to the 3D reciprocal-lattice points. Although the diffraction patterns without an energy filter include Kikuchi lines and Kikuchi bands, the simple conversion is sufficient for determining the crystal structure and orientation. Using this φ-scan RHEED analysis, recently, our group successfully discriminated an α-FeSi2 phase from a c-FeSi phase on Si(001), which are almost indistinguishable in a two-dimensional (2D) RHEED pattern. This was one of the most complex cases, since some transmission diffraction spots almost disappeared owing to the elongated island shape. In this study, we applied this analysis technique to another complex case, aluminum grains on Si(111), having multiple domains with unexpected orientations.

A schematic of the reciprocal lattice of fcc-Al is represented in Fig. 2, where reciprocal-lattice points exist only when h, k, and l are all even or odd. Here, we define the hkl of reciprocal-lattice points O, P, Q, R, S, T, U, and V as [000], [002], [022], [111], [202], [222], [131], and [133], respectively. The reciprocal-lattice unit length a_{Al}^* is 1.55 Å⁻¹ under the definition of 2π/a_{Al}, where a_{Al} = 4.05 Å is the lattice constant of fcc-Al at room temperature (RT). In an fcc crystal, multiple diffraction does not lead to diffraction spots except for the above hkl.

The formation of Al films on Si surfaces has been of interest, since Al is a contact material in Si-based integrated circuits. The epitaxial growth of Al(111) films at RT was reported on Si(111) surfaces by vacuum depositions, with the in-plane relation of Al[110] || Si[110] or Al[110] || Si[110] in many cases. In a few grains — or entire films depending on the treatment conditions, such as different Si surface preparations, substrate heating during the deposition, post-annealing procedures, and so on — various orientations were reported; for instance, Al[111] || Si[111] with Al[110] || Si[110] or Al[110] || Si[110] and Al[001] || Si[111] with Al[110] || Si[110]. These studies utilized
electron diffraction in TEM mainly, and thus their analyses were performed from a few highly symmetric diffraction patterns with restricted directions of the electron beam incident on the milled samples. These analyses perhaps overlook other crystal orientations, since their diffraction patterns display restricted reciprocal-lattice points on an Ewald sphere. This paper shows the existence of other patterns display restricted reciprocal-lattice points on an Ewald sphere. This paper shows the existence of other crystal orientations, Al(001), Al(012), and Al(011) || Si(111), with Al[100] || Si(011), through the 3D reciprocal-lattice mapping.

2. Experimental Procedure
Sample preparations and \( \phi \)-scan RHEED measurements were performed in an ultra-high vacuum (UHV) system with a conventional RHEED equipment and a manipulator realizing an azimuth rotation of a sample stage, which can be cooled by a He refrigerator. A Si(111) sample cut from a mirror-polished wafer (~0.5 mm thick, Sb doped, \(~0.02 \, \Omega \, \text{cm}\)) into \(~4 \times 26 \, \text{mm}^2\) was mounted on a sample holder and introduced to the stage. The samples were degassed and flashed at \(~1250^\circ\text{C}\) by direct current heating below \(4 \times 10^{-8}\, \text{Pa}\) in vacuum. The clean \(7 \times 7\) reconstruction and substrate orientation were confirmed by the RHEED patterns. Aluminum was deposited from an evaporator on the Si(111) \(7 \times 7\) surfaces at \(~40\, \text{K}(\text{LT})\) at an amount of 7 Å estimated by a thickness monitor.

The Al (7 Å)-deposited Si samples were annealed at \(600\, ^\circ\text{C}\) for 5 min. The surface morphology of the annealed samples was observed with an \textit{in situ} scanning tunneling microscope (STM; Unisoku USS-3000) at RT connected to the UHV transfer system\(^{15}\) without exposing the samples to the atmosphere. For a 3D reciprocal-lattice mapping, 205 RHEED patterns at 15 keV in the incident energy were stored in the azimuth range of \(90^\circ\) by \(0.44^\circ\) steps from the Si[112] incidence to the Si[110] incidence for the annealed sample at LT. The typical acquisition time of the 3D RHEED patterns is \(10-20\, \text{min}\) using a 16-bit charge-coupled device camera. To reduce the background from the direct beam spot, the movable beam-stopper was sometimes used. Since the sample stage was weakly magnetized, the position of the direct beam on the screen was slightly moved during the azimuth rotation, that is, the origin of the RHEED patterns was slightly moved, which deformed a 3D reciprocal-lattice map from a simple geometrical conversion (Fig. 1). Thus, a much more accurate 3D reciprocal-lattice map was achieved here by tracking the direct beam position — in a program the obtained patterns were numerically shifted on the virtual screen to locate the direct beam at a fixed position.

3. Results and Discussion
The STM images showed randomly distributed grains \(~5-20\, \text{nm}\) in size and a few nm in height on the Al (7 Å)-deposited and annealed Si(111) surfaces. A typical STM current-image is shown in Fig. 3 with a sample bias voltage of \(+2\, \text{V}\) and a tunneling current of \(0.15\, \text{nA}\). The shapes of the grains were less anisotropic. When the grains are crystals, this implies that all grains can display their own transmission RHEED spots, since their size is less than the inelastic mean free path (\(~20\, \text{nm}\)) of the RHEED electron beam. In RHEED, almost the same transmission patterns were reproducibly obtained at the same incident directions for the different samples. Typical 2D RHEED patterns are shown in Figs. 4(a) and 4(b) at the Si[01\(\bar{1}\)] and Si[11\(\bar{2}\)] incidences, respectively, with a glancing angle of \(~0.1^\circ\). Figure 4(a) displays some transmission spots on rings, the center of which is the direct-beam position. Since the transmission spots appear only close to the direct-beam spot owing to the finite radius (\(62.8\, \text{Å}^{-1}\)) of the Ewald sphere, it is difficult to recognize other spot positions used to assign crystal structures and orientations from this pattern only. Figure 4(b) displays mirror-symmetric and characteristic transmission spots. Since the substrate has a three-fold symmetry, RHEED patterns at the Si[11\(\bar{2}\)] incidence are equivalent to those at the Si[21\(\bar{1}\)] incidence. Thus, Fig. 4(b) corresponds to the perpendicular side of Fig. 4(a). Although the spots seem to be ordered in Fig. 4(b), the lack of spot information on another side [Fig. 4(a)] makes the spot assignment difficult.

The cross sections of the 3D reciprocal-lattice map obtained from the \(\phi\)-scan RHEED measurement are shown in Figs. 4(c)–4(f), and their interpretations in Figs. 4(g)–4(j), respectively. Figure 4(c) shows the top view of the map at the height of line DD in Figs. 4(h)–4(j). Figures 4(d)–4(f) show the side views at lines AA, BB, and CC, respectively, in Fig. 4(g). The substrate azimuth notations are shown...
in Fig. 4(c), with the notations of the reciprocal-lattice rods of Si(111)\(\times 1\). The reciprocal-lattice unit length of Si(111)\(\times 1\), \(a_0\), is 1.89 Å\(^{-1}\), estimated from the real-space unit length \(a_0 = 3.84\) Å at RT. High backgrounds in the cross sections, particularly in Figs. 4(e) and 4(f), are produced by the motion of the direct beam, which was not obstructed by the beam stopper.

We can recognize much more detailed features in the cross sections [Figs. 4(c)–4(f)] than in the 2D RHEED patterns [Figs. 4(a) and 4(b)]. First, we note that reciprocal-lattice rods appear clearly in the side-view cross sections [Figs. 4(d)–4(f)], originating from a substrate Si(111)\(\times 1\).

The side-view cross section at line AA [Fig. 4(d)] clearly shows reciprocal-lattice points on rings even far from the origin, compared with the corresponding pattern in Fig. 4(a). The side-view cross section at line BB [Fig. 4(e)], which cannot have a corresponding pattern in any diffraction method, also shows the characteristic arrangement of reciprocal-lattice points on rings. The side-view cross section at line CC [Fig. 4(f)] shows that the reciprocal-lattice points are aligned on the reciprocal-lattice rods, which looks different from the corresponding pattern in Fig. 4(b).

From the 3D reciprocal-lattice map, we could assign the obtained reciprocal-lattice points to those of fcc-Al with nine
circles, respectively, on plane DD in Figs. 4(h)–4(j). The superposition of the points on plane DD in these orientations is shown in Fig. 4(g). Reciprocal-lattice points $V_{ib}$ and $V'_{ib}$ ($R_{cb}$ and $S_{cb}$) locate above (below) plane DD. Plane $\alpha$ ($\beta$) is determined by the Si[112] [Si[110]] and Si[111] basis directions. Cross sections of points, $U_{1c}$, $V_{1b}$, $R_{2c}$, $S_{2c}$, $V'_{3c}$, and $U'_{3c}$ by the Ewald sphere close to plane $\beta$ having the sphere origin in the Si[112] direction display RHEED spots with the same symbols in Fig. 4(b).

Fig. 5. (Color online) Top views of reciprocal-lattice points in crystal orientations. (a) 1c, (b) 2c, and (c) 3c, represented by blue, cyan, and light-blue circles, respectively, on plane DD in Figs. 4(h)–4(j). The superposition of the points on plane DD in these orientations is shown in Fig. 4(g). Reciprocal-lattice points $V_{ib}$ and $V'_{ib}$ ($R_{cb}$ and $S_{cb}$) locate above (below) plane DD. Plane $\alpha$ ($\beta$) is determined by the Si[112] [Si[110]] and Si[111] basis directions. Cross sections of points, $U_{1c}$, $V_{1b}$, $R_{2c}$, $S_{2c}$, $V'_{3c}$, and $U'_{3c}$ by the Ewald sphere close to plane $\beta$ having the sphere origin in the Si[112] direction display RHEED spots with the same symbols in Fig. 4(b).

Fig. 6. (Color online) Schematics of lattice mismatches in real space for orientations (a) 1c: Al(001), (b) 1b: Al(012), and (c) 1c: Al(011) || Si[111] with (d) Al[100] || Si[011]. Red, green and blue circles represent Al atoms. Black and gray circles represent Si atoms. The interface structures are tentative. Note that the dashed square in (c) is a translational unit.

preferential orientations as follows. The first orientation (named “1a”) is Al[001] || Si[111] with Al[100] || Si[011], some reciprocal-lattice points of which are represented by red circles in Figs. 4(h) and 4(i). Labels $P_{ia}$, $Q_{ia}$, and $R_{ia}$ denote reciprocal-lattice points of this orientation, which are 002, 022, and 111, respectively. Label $O$ denotes the origin of the reciprocal-lattice space. The second (named “1b”) and third (named “1c”) orientations are Al[012] and Al[011] || Si[111] with Al[100] || Si[011], represented by green (e.g., $P_{ib}$, $Q_{ib}$, $R_{ib}$, and $V_{ib}$) and blue (e.g., $P_{ic}$, $Q_{ic}$, $R_{ic}$, and $U_{ic}$) circles, respectively. Symbols $a$, $b$, and $c$ denote the crystal orientations of Al[001], Al[012], and Al[011] || Si[111], respectively. The three-fold symmetry of the substrate can lead to the orientations Al[100] || Si[011], Si[110], and Si[111] denoted by symbols 1, 2, and 3, respectively. The top view in Fig. 4(g) shows such orientations 1c, 2c, and 3c, whose reciprocal-lattice points on cross-sectional plane DD are represented by blue, cyan, and light-blue circles, respectively. For the relationship between the top view and the side views, for instance, note that reciprocal-lattice point $U_{1c}$ on line DD in Fig. 4(i) appears on line BB in Fig. 4(g). The individual orientations in the top view are shown in Figs. 5(a)–5(c), which display some reciprocal-lattice points (e.g., $Q_{1c}$, $U_{1c}$, $Q_{3c}$, $U_{3c}$, and $T_{3c}$) on cross-sectional plane DD in crystal orientations 1c, 2c, and 3c, by blue, cyan, and light-blue circles, respectively. The figures also display some points (e.g., $V_{ib}$, $R_{2c}$, $S_{2c}$, and $V'_{3c}$) out of plane DD. Here, labels $U'$ and $V'$ denote $U_{31}$ and $U_{33}$ in hkl, respectively. In Fig. 4(j), orange circles (e.g., $P_{ia}$ and $S_{ia}$) and light-blue circles (e.g., $Q_{3c}$, $R_{3c}$, and $T_{3c}$) represent some reciprocal-lattice points of orientations 3a and 3c, respectively, with Al[100] || Si[111]. The circles in Figs. 4(g)–4(j) indicate the reciprocal-lattice points expected from these nine orientations. We recognize that almost all spots obtained in Figs. 4(c)–4(f) are well reproduced by the calculated reciprocal-lattice points in Figs. 4(g)–4(j), respectively. The arrangements of the reciprocal-lattice points of the other possible structures and orientations could not reproduce these spots. We could not find twins. Therefore, we consider the formation of fcc-Al with nine preferential orientations.

In this type of multiple-grain system, we should be wary of the direct interpretation from the 2D RHEED patterns, particularly in Fig. 4(b). For instance, some spots, e.g., $S_{2a}$ and $R_{2c}$, in Fig. 4(b) originate from crystals 2a and 2c, respectively, being symmetric to mirror-plane $\alpha$, which is determined by the Si[112] and Si[111] basis directions in Fig. 5(b), while some spots, e.g., $V_{ib}$, $U_{1c}$, $V'_{3c}$, and $U'_{3c}$, originate from crystals 1b, 1c, 3b, and 3c, respectively, not being symmetric to this mirror-plane $\alpha$. That is, spots $S_{2a}$ and $R_{2c}$ correspond to reciprocal-lattice points on plane $\beta$, which is determined by the Si[110] and Si[111] basis directions in Fig. 5(b), while spots $V_{ib}$, $U_{1c}$, $V'_{3c}$, and $U'_{3c}$ correspond to reciprocal-lattice points out of plane $\beta$. Spots $V_{ib}$–$U_{ib}$ appear in Fig. 4(b) owing to the finite (but close to plane $\beta$) Ewald-space radius with the sphere origin in the Si[112] direction. In other words, reciprocal-lattice point $T_{3c}$ in Fig. 4(j) does not appear as a 2D-RHEED spot at the Si[121] incidence owing to the finite Ewald radius, as shown in the corresponding pattern in Fig. 4(b). We emphasize that such spot assignments are possible only after the 3D reciprocal-lattice mapping.

All crystals with the common axes Al[100] || Si[011] can be expressed as Al[01n] || Si[111], when $n = \infty$, 2, and 1 correspond to orientations $a$ [Al[001]], $b$ [Al[012]], and $c$ [Al[011]], respectively. The existence of the common axes, Al[100] || Si[011], may suggest a strong bonding in these directions, but the lattice mismatch in these directions is not small (+5.5%, $a_{Al}/a_{Si} = 4.05\ Å/3.84\ Å$). The lattice mismatches of the crystals with $n = \infty$, 2, and 1 are small in the other perpendicular in-plane Si[111] directions as +1.5% ($5a_{Al}/3\sqrt{3}a_{Si}$), +2.1% ($3\sqrt{5}a_{Al}/4\sqrt{3}a_{Si}$), and +0.5%
[(7/2)\sqrt{2a_{Al}}/3\sqrt{3a_{0}}], respectively. The schematics of the lattice mismatches are shown in Fig. 6. For the other possible orientations with integer \(n\), the coincidence of Al and Si lattices requires a longer distance and may become unstable. Since the preparation conditions are different from those indicated in previous reports, where a large amount (larger than several-hundred Å) of Al was deposited, our new crystal orientations of fcc-Al on Si(111) surfaces would act as the initial stage of nucleation growth.

4. Conclusions

Using a novel analysis method for crystal structures and orientations by 3D reciprocal-lattice mapping from azimuth-scan RHEED patterns, we successfully determined the crystal orientations of fcc-Al multiple grains formed on a Si(111) surface. There are nine preferential orientations with the three different Al-planes having the three-fold symmetry in each caused by the substrate, Al(001), Al(012), and Al(011) || Si(111) with Al[100] || Si[011]. This determination is hard to realize from a few diffraction patterns. The \(\phi\)-scan RHEED can be easily applied in \textit{in situ} vacuum-fabricated nanocrystals on substrate surfaces with high sensitivity. The typical acquisition time of 3D RHEED patterns is 10–20 min, which is shorter than many hours of a standard X-ray diffraction system with \(\phi\) and \(\omega\) scans. We emphasize that the 3D reciprocal-lattice mapping by this \(\phi\)-scan RHEED analysis has an excellent capability of finding all crystal phases and orientations of nanocrystals, especially for the initial stage of device fabrication.

16) The lattice mismatches using multiple lattice units of a film and a substrate generally described. For instance, the TEM images clearly show the matching of every four Al(112) planes to three Si(112) planes at interfaces, \(4(\sqrt{2}a_{Al})/3\sqrt{3}a_{0}\) leading to \(-0.6\%\). In our case in Al[100] || Si[011], few mismatches (\(\lesssim 5.5\%\)) are possible for longer matching distances (\(\gtrsim 7.7\) nm \(\approx 10a_{Al} \approx 20a_{0}\)), however, which are unrealistic.