REFLECTION HIGH-ENERGY ELECTRON DIFFRACTION

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INTRODUCTION

Reflection high-energy electron diffraction (RHEED) uses a finely collimated electron beam with energy of 10–100 keV. The beam irradiates a sample surface with grazing incidence to obtain forward scattered diffraction patterns. RHEED enables us to analyze structures of crystal surfaces at atomic levels and also to in situ monitor growth processes of thin films (Ino, 1988; Ichimiya and Cohen, 2004; Peng et al., 2011). From the arrangement, intensity and profile of the diffraction spots in RHEED patterns, as described below in detail, one can obtain various kinds of information; (1) the periodicity (unit cells) in atomic arrangements, (2) flatness of surfaces, (3) sizes of grains/domains of surface structures and microcrystals grown on the surface, (4) epitaxial relation between the grown films/islands with respect to the substrate, (5) parameters characterizing structural phase transitions, (6) individual atomic positions in the unit cells, and (7) growth styles of thin films and numbers of atomic layers grown.

The most important advantages of the method are that it is quite easy to install the RHEED apparatus in various types of vacuum chambers without interfering with other components of apparatuses and to do realtime monitoring during thin-film growths. Because of these advantages, RHEED is now widely used not only in research labs of surfaces and thin films, but also in device production processes in industry.

Low-energy electron diffraction (LEED, see article Low-ENERGY ELECTRON DIFFRACTION), in which an electron beam of 10–100 eV in energy is irradiated onto a sample surface with nearly normal incidence to obtain backscattered diffraction patterns, is also widely used to analyze the atomic structures of crystal surfaces. Since one has to make the sample face directly to the LEED optics, resulting in that the space in front of the sample surface is almost occupied by the LEED apparatus, it is not easy, compared to RHEED, to combine LEED with other instruments for simultaneous crystal growth and other analysis methods in vacuum chambers. If, furthermore, the sample is heated at high temperatures to become shining, it is difficult to see the LEED pattern due to the light from the heated sample. The light from the heated sample, in contrast, does not disturb the RHEED observation, because the screen for the pattern observation is far away from the sample and does not face the sample surface. Because of these simple reasons coming from the geometrical arrangement of apparatuses, LEED is usually used for static analysis of surface structures without combining other methods for analysis and crystal growth, while RHEED is more suitable to analyze and monitor dynamical changes of structures during sample heating, deposition/desorption of species on/from the sample, crystal growth, and so on. Therefore, RHEED is usually installed in vacuum chambers of thin-film growth such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) methods.

Transmission electron diffraction (TED), in which an electron beam of 50-100 keV in energy is irradiated onto a thin sample with nearly normal incidence to obtain forward-scattered diffraction patterns in transmission mode in a transmission electron microscope (TEM), is also utilized for structure analysis of surfaces and thin films (Takayanagi et al., 1985). This can be easily combined with usual TEM observations to obtain information in both of direct and reciprocal spaces of an aimed area of the sample. And because of the high energy and thinness of the sample, multiple scattering of electrons can be neglect in TED, which makes the quantitative analysis easier than in LEED and RHEED. Multiple scattering (dynamical effect) is usually significant in LEED and RHEED. But, in TED, one needs to prepare thin samples enough for the electron beam to transmit through, which is not easy for every sample, while bulky samples can be used in LEED and RHEED because of the reflection mode.

RHEED uses an electron beam of high energy enough to excite secondary electrons, Auger electrons (Horio and Ichimiya, 1983), and x-ray (Hasegawa et al., 1985) from the sample surface, which enables simultaneous analysis of chemical composition and atomic-bonding states in the beam-irradiated area by analyzing the energy of the excited electrons and x-ray. These are useful secondary techniques that can be combined with atomicstructure analysis by RHEED. RHEED can be carried out by using the electron beam of nanometer-order diameter in scanning electron microscope (SEM) to obtain a kind of real-space micrograph. This is so-called scanning REM (reflection electron microscopy) and micro-beam RHEED (Ichikawa et al., 1984). RHEED can also be performed in a transmission electron microscope in a reflection mode, which is called REM (Yagi, 1993). Information of local structures on surfaces both in direct and reciprocal spaces is obtained by these methods.

This article describes fundamentals of RHEED, its apparatus, analysis methods, and information provided by RHEED by showing some examples. Since the fundamentals of electron diffraction are not fully described here, the readers should consult textbooks for it.

PRINCIPLES OF THE METHOD

Figure 1 illustrates the apparatus of RHEED. The electron beam, produced and accelerated in an electron gun, passes through a small aperture, and is focused on a fluorescence screen by a (magnetic) focusing lens. The divergence angle of beam is usually less than 10^{-4} rad and the diameter of focused spot on the screen should be less than 0.1 mm. The beam is deflected by deflection coils Nos. 1 and 2 to irradiate the sample surface with a defined glancing angle θ_g (the complementary angle of incidence angle). The θ_g should be as small as 0.5–6°. Since the θ_g is so small, the irradiated area on the sample surface is 1–3 mm long along the beam. Therefore, the information from RHEED is usually an average and sum in such a macroscopic area.

Since the glancing angle θ_g of electron beam is a very important parameter in RHEED to define specific diffraction conditions, the angle should be adjusted very finely by inclining the sample with respect to the beam or by using double deflection coils (Nos. 1 and 2). Another important parameter is the azimuth angle of beam incidence with respect to crystal orientation. It is more desirable, therefore, to be able to rotate the sample azimuthally around the surface normal direction. The



Figure 1. Schematic diagram of RHEED apparatus.

glancing and azimuth angles are important to select specific diffraction conditions such as so-called *surfacewave resonance* condition (in which multiple scattering is enhanced at the surface region to increase the surface sensitivity) and *one-beam condition* (in which multiple scattering is suppressed to make the quantitative analysis easier) (Ichimiya and Cohen, 2004).

The RHEED pattern is observed on the fluorescence screen which is placed inside the view port flange of the vacuum chamber, and can be recorded by photo or a CCD camera from the outside. The spot intensity and profile are analyzed later from the stored images or in real time with a CCD-PC system. Alternately, the spot intensity can be measured directly as current by a Faraday cage, a small metal cage to collect the aimed diffracted beam only, which is connected to a picoammeter.

Recently, PC-based real-time data processing of RHEED pattern is widely used. The integrated intensity, peak intensity, and profile of the selected spots (with appropriate background subtraction), and spot spacing between the aimed spots are automatically measured and stored in real time.

Ewald Construction

Figure 2a shows schematically the relation between the geometrical arrangement in RHEED (drawn upside down) and the reciprocal space (momentum space). In general, so-called *Ewald construction* described below is frequently used for intuitive understanding of diffraction phenomena. k_0 is the wavevector of the incident electron wave. Since we restrict ourselves to elastic scattering only, the diffracted waves, for example, k_1 and k_2 , have the same magnitude of wavevectors as k_0 . Therefore, when these vectors are drawn from the common origin with that of k_0 , their end points are on a sphere with its radius $|k_0|$. This is called as a *Ewald sphere*.

When the sample is assumed, as shown in Figure 2a, to be atoms arranged equidistantly on a line along the

incident beam, the Fourier transform of this atom row is a series of equidistant planes (reciprocal lattice planes) perpendicular to the atom row. Intersections between the Ewald sphere and the reciprocal lattice planes are a series of circles. The vectors from the center of Ewald sphere, which is the common origin of the wavevectors, to the circles are wavevectors of the diffracted waves, for example, k_1 and k_2 . This process for constructing the figure ensures both of the elastic scattering and diffraction conditions fulfilled simultaneously. The circles are actually observed on the fluorescence screen as concentric circles (though only the half of circles above the shadow edge is observed on the screen). The smallest circle is called as the 0th Laue zone (L_0) , and the next one is the 1st Laue zone (L_1) . The circles are slightly distorted near the shadow edge because of the refraction effect of electron beam.

A surface of a square-lattice crystal, for example, is regarded as a combination of the atom rows mentioned above and their 90°-rotated atom rows. Therefore, its reciprocal lattice is intersections between two series of equidistant planes rotated by 90° with each other. This is a set of rods. The *reciprocal rods* are arranged in square equidistantly, and stand perpendicularly to the sample surface. Consequently, the intersections between the Ewald sphere and the reciprocal rods are points, which appear as *diffraction spots* on the screen. The diffraction spots in RHEED patterns from a twodimensional (2D) lattice are thus always on the circles (Laue zones).

Figure 2b is an example of RHEED pattern, which is taken from a clean Si(1 1 1)–(7 × 7) reconstructed surface. All diffraction spots are on the concentric circles as mentioned above. On the 0-th Laue zone (L_0) and the 1st Laue zone (L_1), one can find stronger spots, called as *fundamental spots*, which comes from the diamondlattice structure of the bulk Si crystal (the electrons are scattered not only from the topmost atomic layers, but also from a region of several atomic layers deep below the surface). Between the fundamental spots, there are



Figure 2. (a) Direct space and reciprocal space of RHEED. (b) RHEED pattern taken from a Si(1 1 1)–(7 × 7) reconstructed surface. The electron beam was 15 keV in energy with $[11\overline{2}]$ incidence in azimuth direction and about 3° in glancing angle θ_g to attain a surface-wave resonance condition.

many fine spots, superlattice spots (or fractional-order spots), which originate from the reconstructed surface structure having a larger unit cell than in the bulk crystal. The spacing and arrangement of the superlattice spots, with reference of the fundamental spots, tell us the periodicity or the size/shape of the unit cell of the reconstructed surface structure. One can notice, furthermore, that the intensity is not equal among the superlattice spots. The electron waves, scattered from individual atoms, interfere with each other to make some diffraction spots stronger or weaker depending on the path differences. Therefore, the spot intensity distribution is important information for analyzing individual atom positions in the unit cell. This is structure analysis by electron diffraction, much like x-ray structure analysis for bulk crystals.

Coherence Length

The spatial resolution in RHEED structure analysis, which is usually 0.01–0.001 nm in shifts of atom positions, is determined by the coherence length of electron beam used. The coherence length, in which the scattered waves interfere with each other by keeping the phase information, is determined by how much monochromatic the energy of electron beam is and how much parallel the beam is. That is, the coherence length ℓ is defined by the energy speared ΔE and the divergence angle $\Delta \theta$ of the electron beam by

$$\ell = \frac{\lambda}{\sqrt{2(\Delta\theta)^2 \sin^2 \alpha + \left(\frac{\Delta E}{E}\right)^2 \cos^2 \alpha}}$$
(1)

where λ is the wavelength of electron wave, and α is the angle between the incident electron beam and the direction for measuring the coherence length. The coherence length along the beam ($\alpha = 0^{\circ}$), the *longitudinal coherence length* ℓ_L , is determined by the energy spread ΔE of the electron beam only. The coherence length perpendicular to the beam ($\alpha = 90^{\circ}$), the *transverse coherence length* ℓ_T , is determined by the divergence angle $\Delta\theta$ of the beam only.

$$\ell_L = \lambda \left(\frac{E}{\Delta E}\right) = \frac{\lambda^2}{\Delta \lambda}, \ \ell_T = \frac{\lambda}{\sqrt{2}\Delta\theta}$$
 (2)

For usual thermal-emission electron beams generated from a heated tungsten filament in RHEED at 10 keV acceleration, $\ell_L = 100-200$ nm and $\ell_T = 30-80$ nm, which are about 5–10 times longer than those in LEED. Therefore, RHEED "observes" a much larger area on the surface than LEED, and the resolution in determining the atom positions is higher. Note that the scattered waves from areas of size of coherence length (about 100 nm) interfere with each other coherently while the scattered waves from the whole irradiated area (about 0.1 mm) are summed up incoherently.

One can notice bright straight line/band features in the RHEED pattern in Figure 2b. They are called as *Kikuchi lines/bands*, (see article TRANSMISSION ELECTRON MICROSCOPY) originated from inelastic scattering process. They provide information of crystal symmetry and orientation.

PRACTICAL ASPECTS OF THE METHOD

Actual samples are not always ideal; the surface is not atomically flat, or the surface has finite size of domains, much like polycrystals, whose size is smaller than the coherence length of electron beam. The RHEED patterns then suffer various modifications due to such imperfections of the samples.

Figure 3 illustrates some cases. When the sample has an atomically flat surface and a perfect single-crystalline structure as shown in Figure 3a, its reciprocal rods are very sharp without intensity modification along the rods under an assumption that the RHEED detects the topmost atomic layer only. Then the diffraction pattern is a reflection type in which all diffraction spots are on the Laue zones and have the same intensity, as mentioned in Figure 2. In reality, however, the electron beam penetrates into several atomic layers below the surface. Then the intensity is modulated along the reciprocal rods, resulting in that some diffraction spots are stronger and others are weaker. This is due to interference among waves scattered from different atomic layers.

As shown in Figure 3b, when the surface is composed of small out-of-phase domains whose size is smaller than



Figure 3. Schematics of various kinds of realistic surfaces, in real-space morphology, in reciprocal space, and their RHEED patterns (courtesy by Yoshimi Horio).

the coherence length of electron beam, the reciprocal rods are broader due to effect of the Laue function for finite sample sizes. The width of the reciprocal rods is inversely proportional to the average size of the domains. Then, the intersections between the Ewald sphere and the reciprocal rods become larger ellipses, resulting in elongated and broader diffraction spots (streaks) in the RHEED pattern. Inversely, from the width and length of the streaky spots, we can estimate the average size of domains.

As shown in Figure 3c, when the surface is rough by two-level terraces with one-atomic height difference, the reciprocal rods become a bit complicated. Under the on-Bragg condition where the electron waves reflected from the lower and upper terraces interfere with each other constructively, the electron beam does not "see" the twolevel roughness, so that the reciprocal rods are sharp as those of the atomically flat surfaces. On the other hand, under off-Bragg conditions where the waves reflected from the lower and upper terraces interfere destructively, the intensity of the diffracted beam is weak. The intensity is proportional to the difference in area fraction between the lower and upper terraces. And the reciprocal rods are split into two, of which lateral spacing is proportional to the average width of terraces: the terraces act as a grating for the electron wave. As a result, the diffraction spots are also spit into satellite spots/ streaks. From the spacing of the satellite streaks, we can estimate the average terrace width.

As shown in Figure 3d, when the surface is rough with multilevel terraces of different widths, the reciprocal rods are modulated as shown in the figure because they are regarded as superpositions of those in Figure 3c with various spacing of split rods at the off-Brag conditions. Then, the reciprocal rods have sharp "nodes" with strong intensity at the on-Bragg points, while they become broader and weaker at the off-Bragg portions. This produces RHEED patterns having elongated streaks with intensity modulation in the perpendicular direction.

As shown in Figure 3e, when the crystal is cut with some angle from a low-index crystal orientation, the surface has morphology of a staircase with regular step arrays. When the terrace width is smaller than the coherence length of electron beam, the reciprocal rods are again a bit complicated. The rods are perpendicular to the surface of terraces, and broader at the off-Bragg conditions because of the narrow width of the terraces, like in Figure 3c. The rods, however, contain finer rods inside. The fine rods are perpendicular to the overall surface of the sample which is slightly inclined from the terrace surface. The spacing between the fine rods is inversely proportional to the average terrace width. As a result, the diffraction spots become inclined satellite streaks.

As shown in Figure 3f, when the surface is rough with three-dimensional islands, and when the glancing angle of electron beam is small, the electron beam transmit through the protruded parts of islands and produces a transmission diffraction pattern, which is not a reflection pattern any more. When the islands are epitaxially grown on the surface, the reciprocal lattice is the same as that of three-dimensional crystal, which is three-dimensional array of reciprocal points. The diffraction pattern is then usual ones from 3D crystals. When the islands have crystal facets on the side walls, small streaks, which are reflections from the facets and therefore perpendicular to the facets, appear around the diffraction spots. When the islands are nonepitaxial with respect to the substrate surface in which the crystal orientation of the islands are random, one obtain a Debye–Scherrer ring pattern where the diffraction spots in Figure 3f are rotated around the direction of electron beam.

Figure 4 shows some examples of RHEED patterns (Hasegawa et al., 1987), taken during Ag deposition on Si(1 1 1)–(7 \times 7) reconstructed surface (a). At room temperature, Ag atomic layer grows without destroying the 7 \times 7 structure, and streaks from the Ag layers begin to appear as seen in (b). With three monolayers (ML) deposition (c), the surface is fully covered by Ag layers and the 7 \times 7 superlattice spots disappear. The streaks show some intensity modulation, much like that in Figure 3d, meaning that the surface of Ag layer is rough with multilevel stepped terraces.

By deposition of Ag at 440°C, on the other hand, the Ag adsorption induces a structure conversion from the 7×7 to $\sqrt{3} \times \sqrt{3}$ reconstructed structure. With a half monolayer adsorption (d), some areas on the surface are the $\sqrt{3} \times \sqrt{3}$ domains while other portions remain the 7×7 domains, so that the RHEED pattern is a superposition of the two reconstructed structures. By a full monolayer deposition (e), the surface is fully converted into the $\sqrt{3} \times \sqrt{3}$ reconstructed structure. The $\sqrt{3} \times \sqrt{3}$ superlattice spots are much more elongated than those of the 7×7 superlattice spots, meaning that the $\sqrt{3} \times \sqrt{3}$ domains are much smaller (a few nanometers in average size) than the 7×7 domains (around 100 nm in size), as mentioned in Figure 3b.

Figure 5 shows another example of RHEED patterns, obtained from Al deposits on Si(111) surface, showing a melting-crystallization transition of Al microcrystals (Hasegawa et al., 1995). Figure 5a was taken after deposition of Al of about 20 ML onto Si(1 1 1)–(7 \times 7) reconstructed surface at room temperature. The spots were not arranged on Laue zone, and did not change even when the sample was rotated azimuthally around the surface normal direction. This means that this is a transmission pattern from 3D islands/microcrystals, as shown in Figure 3f. By analyzing the lattice constant and reciprocal lattice of bulk Al crystal, the pattern says that the Al islands are epitaxially grown in that $(1\ 1\ 1)_{Si}$ $(001)_{Al}$ with two kinds of azimuthal orientations $\langle 11\bar{2}\rangle_{\rm Si}//\langle 010\rangle_{\rm Al}$ and $\langle 1\bar{1}0\rangle_{\rm Si}//\langle 010\rangle_{\rm Al}$. The broad spots mean that the Al islands are very small (on the order of a few nm). On heating this sample, the Al islands melt at around 684°C, showing a halo pattern as in Figure 5b. This indicates a radial distribution function in the molten Al. When the sample is cooled down, the Al began to recrystallize around 655°C, resulting in a kind of Debye-Scherrer ring pattern as in Figure 5c, which is again a transmission diffraction pattern of Al microcrystals. This means that Al microcrystals are 3D and grown in random orientations on the Si surface. When this sample was then heated up again, the pattern changed



Figure 4. RHEED patterns observed during Ag deposition onto Si(1 1 1) –(7 \times 7) reconstructed surface (**a**) at room temperature (**b**)(**c**) and at 440°C (**d**) (**e**). The amount of Ag deposited is (b) 1.5 ML, (c) 3.0 ML, (d) 0.5 ML, and (e) 1.0 ML. ML (monolayer) means a single-atomic layer. Reprinted from (Hasegawa et al., 1987), Copyright 1987, with permission from Elsevier.

from Figure 5c and d just before melting, in that the intensity of the spots from Al microcrystals in some preferential orientations increased at the cost of the ring intensity. This means that the Al microcrystals align themselves along particular orientations. By slightly further increase of temperature, the Al microcrystals melt again, and the RHEED pattern returned to Figure 5b.

DATA ANALYSIS AND INITIAL INTERPRETATION

Since the RHEED pattern is distorted due to its geometrical arrangement, one needs a transformation from the pattern to the two-dimensional (2D) reciprocal lattice (corresponding to a LEED pattern) with help of a figure shown in Figure 6b. This is an example with Si $(1 \ 1 \ 1)$ - (7×7) reconstructed surface (Fig. 6a). Since this

surface is a (111) plane of a diamond-lattice crystal, the 2D fundamental reciprocal lattice points should form a hexagonal lattice as shown by open circles in the lower part of Figure 6b. Because the incidence azimuth is $[11\bar{2}]$ in this case, the indexes of the fundamental spots are O (0,0), C(1,1), B(0,1), D(1,2), E($\overline{1},\overline{1}$), and so on. Since, as mentioned above, all diffraction spots are intersections between the Ewald sphere and the reciprocal lattice rods which stand perpendicular to the shadow edge, straight lines perpendicular to the shadow edge are first drawn from the fundamental spots to form the hexagonal reciprocal lattice. Its unit cell is made of the reciprocal lattice vectors \vec{a}^* and \vec{b}^* . Next, straight lines from the superlattice spots are also drawn in the same way to make reciprocal points (filled circles) in the 2D reciprocal lattice by referring to the fundamental reciprocal points (open circles). As a result, the unit cell of the surface reconstructed structure is a small lozenge whose side is



Figure 5. RHEED patterns from a surface (**a**) after a room-temperature deposition of 20 ML Al onto Si(1 1 1) $-(7 \times 7)$, (**b**) after melting of the Al by heating, (**c**) after its recrystallization by cooling, and (**d**) after heating again up to just below the melting temperature, respectively. The changes in the patterns (b) \Rightarrow (c) \Rightarrow (d) \Rightarrow (b) are repeated in the cooling-heating cycles around the melting temperature. Reprinted from (Hasegawa et al., 1995) with permission from Taylor & Francis Ltd.

1/7 of the fundamental unit cell. This means that the unit cell of the reconstructed structure in direct space is seven times larger in both of \vec{a} and \vec{b} directions than the fundamental unit cell of the Si(1 1 1) crystal face. Therefore, the surface is called by a 7×7 superstructure.

In this way, the RHEED pattern is transformed into a 2D reciprocal lattice to know the periodicity or size/ shape of unit cell of surface reconstructed structures, even though the atomic arrangement within the unit cell is unknown. The positions of individual atoms in the 7×7 unit cell are now known according to a so-called dimer-adatom-stacking-fault (DAS) structure model (Takayanagi et al., 1985), which has been obtained by analyzing the intensity of superlattice spots.

An expert of RHEED can recognize the 2D reciprocal lattice directly from the RHEED pattern without drawing a figure like Figure 6b.

As seen in Figure 2a, the shadow edge is a projection from the sample surface, below which is the shadow of the sample. The fundamental spots C and E in Figure 6a, which are on the shadow edge, are, therefore, produced by electron beams diffracted parallel to the sample surface. In other words, the strong electron waves propagate along the surface, meaning that the electron waves do not penetrate deeply into the crystal. This ensures a high sensitivity to the surface layer. Such waves are then diffracted mainly by the surface reconstructed structure to enhance the intensity of the superlattice spots. This situation is called as surface wave resonance (or Kikuchi-Nakagawa effect). Although this makes the superlattice spots very intense to produce a beautiful RHEED pattern, multiple scatterings occur at the surface layer, which makes the quantitative analysis of spot intensity very difficult. Therefore, this condition is selected only for taking photos of beautiful RHEED patterns, but avoided in rocking curve analysis for structure determination.

Another example of RHEED pattern is shown in Figure 6c, taken from a Si(111)-5 \times '2'-Au reconstructed surface. This surface is prepared by depositing a half atomic-layer thick Au on the Si(111)– (7×7) surface kept around 500°C. The superlattice spots cut the line between O and B into five parts as shown in Figure 6d, while a streak bisects the line between O and C. This means that the fivefold periodicity in \vec{b} direction is perfect, while the double periodicity in \vec{a} direction is imperfect. This is a structure in direct space that one-dimensional chains having a double-fold periodicity (2a) along the chain are aligned every five-time spacing (5b), without correlation among them in the chain direction (Daimon et al., 1990). So the surface is called a $5 \times 2'$ structure with quotation marks on 2.

In this way, the periodicity or unit cell of the surface reconstruction structure is known simply from the arrangement of the superlattice spots in RHEED pattern.

Phase Transitions

Figure 7 shows an example of RHEED observation of a structural phase transition (Hasegawa et al., 1993). The superlattice spots from Si(1 1 1)–(7 × 7) reconstructed surface, which are clearly observed at room temperature as shown in Figure 7a, become weaker by raising the temperature (Fig. 7b), and eventually disappear at around 800°C (Fig. 7b), leaving the fundamental spots only to be a 1×1 structure. However, the superlattice spots recover by cooling down the sample to return to the 7×7 structure. Therefore, this process is a reversible temperature-induced phase transition in which only the 7×7 reconstructed structure in the topmost atomic layers melts into a disordered phase without melting in the diamond lattice of bulk Si below the surface layer (Kitamura et al., 1991).





Figure 6. (a) RHEED pattern taken from Si(111) -7×7 reconstructed surface. (b) Its interpretation into 2D reciprocal lattice. (c) RHEED pattern of Si(111) -5×2^{-4} -Au reconstructed surface, and (d) its interpretation.

Figure 7d shows the integrated intensity of the (1/7, 3/7) superlattice spot (indicated by white arrow heads in Fig 7a and b) during heating and cooling around the phase transition temperature. One can recognize a hysteresis by about 5°C between the heating and cooling processes. The inset shows line profiles of the spot as a function of temperature, showing negligible change in the full width of half maximum of the spot. This means no critical scattering, a characteristic of the second-order phase transition. From these results, one can say that the melting transition of $7 \times 7 \iff 1 \times 1$ is a first-order phase transition.

For comparison, another phase transition in which Si $(1 \ 1 \ 1)$ - β - $\sqrt{3} \times \sqrt{3}$ -Au reconstructed surface structure melts, is shown in Figure 7e (Hasegawa et al., 1993). This

surface is prepared by depositing a monatomic-layer Au on the Si(1 1 1)–(7 \times 7) surface kept around 500°C. The (1/3,1/3) superlattice spot disappears around 750°C, but no hysteresis is observed between the heating and cooling processes. The inset shows line profiles of the spot as a function of temperature, showing that the tail expands just before the spot disappears. This is a critical scattering showing a growth of short-range order around the phase transition. Therefore, we can say that this is a second-order phase transition. The detailed spot analyses in high-resolution LEED have concluded that this transition is categorized as a transition with three-state Potts model (Nakajima et al., 1997).

In this way, the spot intensity and spot profile provide important information characterizing structural phase



Figure 7. RHEED pattern taken from Si(1 1 1)–(7 × 7) surface at room temperature (**a**), 790°C (**b**), and 805°C showing a 1 × 1 structure (**c**). (**d**) Integrated intensity of the (1/7, 3/7) superlattice spot as a function of temperature. (**e**) That of the (1/3, 1/3) superlattice spot of the Si(1 1 1)- β - $\sqrt{3}$ × $\sqrt{3}$ -Au surface. The insets in (d) and (e) are spot profiles at each temperature. (Hasegawa et al., 1993).

transitions. This is common to x-ray and neutron diffractions though they are for bulk structure analyses.

RHEED Rocking Curve Analysis

In order to determine the positions of individual atoms in the unit cell, one has to measure rocking curves $I(\theta_g)$, the spot intensity *I* as a function of the glancing angle θ_g . This is much like LEED I(V) curve measurements in which the spot intensity *I* in LEED is measured as a function of the acceleration voltage *V*. By changing the glancing angle in RHEED (or by changing the electron wavelength in LEED), one can change the diffraction condition and measure the intensity distribution along the reciprocal rods. The diffracted intensity along the rods is a result of interference among many waves scattered from individual atoms in the unit cell in different atomic layers. Therefore, we can analyze the atomic positions from the intensity of diffracted waves.

Once the rocking curves are obtained by experiments, next one has to calculate the intensity distribution along

the rods by assuming a model of the atomic structure in the unit cell, and compare it with the experimental result. If the simulated rocking curves and experimental ones do not match well with each other, one has to change the model and try the calculation again with different models. Such trial-and-error analyses will eventually bring us to the correct atomic arrangement though it takes much time. The simulation is usually done by using dynamical diffraction theory in which multiple scattering is fully incorporated. A reliability factor (R-factor), which is a kind of error function indicating how much the discrepancy is between the experimental and simulated rocking curves, is used as a criterion whether the assumed model is correct or not. With shifting the positions of atoms in the assumed model structure, the reliability factor is calculated to find the best combination of atom positions. The best arrangement of atoms is found when the smallest reliability factor is obtained. When the reliability factor is small enough, we can say that the assumed atomic structure is correct.



Intensity 351 462 573 684 T T 0 1 2 3 4 5 6 Glancing angle (deg) (a) Figure 8 shows an example of RHEED rocking curve analysis (Hanada et al., 1993). The sample is Si(111)– $\sqrt{3} \times \sqrt{3}$ -Ga reconstructed surface which is formed by 1/3 ML Ga adsorption on Si(111) – (7 × 7) surface at about 300°C. The intensities of integer spots and fractional-order spots are measured as a function of the glancing angle of electron beam as shown by solid lines in Figure 8a. Then three kinds of structure models are assumed as shown in Figure 8b; one Ga atom sits in the $\sqrt{3} \times \sqrt{3}$ unit cell though the adsorption site of Ga is unknown. Possible sites are three due to symmetry; T₄ model in which the Ga atom adsorbs above the secondlayer Si atom, H₃ model in which the Ga atom adsorbs on the third-layer Si atom, and S_5 model in which the Ga atom sits above the topmost Si atom. The rocking curves are calculated for the three models by changing a structure parameter h_a , the distance between the Ga-atom layer and the topmost Si layer as shown in Figure 8c. Then, the R-factor is calculated for each model by comparing with the experimental rocking curves. The results are summarized in Figure 8c. The T_4 model with $h_a = 1.5$ Angstrom gives the smallest R-factor. In this way, the adsorption site of Ga atom is determined quantitatively. The dashed curves in Figure 8a are the simulated ones

using the optimized T_4 model. If the minimum value

of R-factor is not small enough even with the

optimized structure parameters, the assumed model

can be wrong.

(arb.units)



Weissenberg RHEED

Recently a new method with RHEED is devised for more systematic and accurate structure analysis. As shown in Figure 9 (Abukawa et al., 2006), many RHEED patterns are collected with changing the azimuth angle ϕ , instead of the glancing angle θ_g , of the incident electron beam. This is much like Weissenberg camera method for x-ray diffraction. Thus, one can obtain the intensity distribution in a wide area of the 3D reciprocal space as shown in Figure 9b. By Fourier transform of the reciprocal data, one can obtain a Patterson map which is an autocorrelation function of the atom arrangement in real space. Therefore, the correct atomic structure can be obtained by a much more direct way than by the trialand-error method of usual rocking curve analysis.

RHEED Intensity Oscillation

RHEED is used to monitor the growth of atomic layers on crystal surfaces by measuring oscillatory changes of the intensity of a specular spot. When the exit angle and glancing angle θ_q of the electron beam are equal as shown in Figure 10a, the reflected beam is called as the specular beam and its spot is the specular spot, which is always enhanced in intensity by constructive interference irrespective of the angle θ_g : since the two paths shown in Figure 10a reflected from the same atomic plane have no path difference, they are always



Figure 9. Weissenberg RHEED, in which many RHEED patterns are collected with changing the azimuth angle ϕ of the incident electron beam (Abukawa et al., 2006).

in-phase and constructively interfere with each other. When an atomic step exits on the crystal surface as shown in Figure 10b, some part of the specular beam is reflected from the upper terrace, while other part is reflected from the lower terrace, resulting in some path difference created between them. By choosing the incident angle θ_g (which equals to the exit angle), the two waves can interfere destructively to diminish the



Figure 10. RHEED intensity oscillation and crystal growth monitor. (**a**) and (**b**) Specular beam from a flat surface and a stepped surface, respectively. (**c**) Illustrations showing a 2D-island growth style and (**d**) the intensity change of specular spot during the growth, reprinted from (Joyce et al., 1986), Copyright 1986, with permission from Elsevier. (**e**) Experimental data of RHEED intensity oscillations during Ge homoepitaxy on Ge(1 1 1) surface (Fukutani et al., 1992).

intensity of the specular beam (off-Bragg condition, or out-of-phase condition). Therefore, one can distinguish between an atomically flat surface and a stepped surface by measuring the intensity of specular spot under the off-Bragg condition with an appropriate glancing angle of beam.

During crystal growth under some condition, the atomic layers grow in a layer-by-layer fashion as shown in Figure 10c (Joyce et al., 1986). The next atomic layer grows by making 2D islands here and there on the surface first, then the islands grow laterally and eventually connect each other to complete the new atomic layer. Thus, the surface temporally becomes a stepped surface during the growth. This process can be monitored by utilizing the intensity change of the specular spot as mentioned above. The intensity should oscillate as shown in Figure 10d during the layer growth; the period of the oscillation corresponds to the completion of growth of a single atomic layer. Therefore, just by counting the number of intensity oscillations of the specular spot in RHEED during, for example, MBE crystal growth, one can know the number of the atomic layers grown. Then one can control the thickness of the grown layer with precision of one-atomic-layer thickness.

Figure 10e shows an example, the intensity changes of the specular spot in RHEED during deposition of Ge onto Ge(111) surface at various temperatures (Fukutani et al., 1992). The period of oscillation is one atomic layer at room temperature. But, the oscillation decays gradually over 10 ML growth, meaning that the surface becomes rough with multilayer levels. At 140°C, in contrast, the oscillation continues for many layers, meaning that the surface remains flat even after growth of many layers. The oscillation period becomes two-atomic layers at 180°C, which means that the crystal grows in a unit of bi-layers of a (111) lattice plane in the diamond crystal structure. The layer-by-layer growth continues for many layers at this temperature. By increasing the temperature further, the oscillation diminishes and eventually disappears at 250°C. This means that the growth style changes from the 2D-island growth (Fig. 10c) to a step-flow type as shown by the inset of Figure 10e in which the step density or the surface roughness does not change during the growth: the impinging Ge atoms are so mobile at high temperature that they can migrate for long distances and are stuck on step edges, resulting in forward movement of step edges without creating new step edges during the growth.

The explanation mentioned above for the RHEED intensity oscillation is a simplest one in a framework of kinematical diffraction, that is, interference of waves diffracted from the upper and lower terraces. This picture works well in general in the case of low step-density. When the step density is so high and the terraces are narrow, however, one cannot ignore the waves diffracted from the step edges where the lattice is somewhat distorted. Multiple scattering effect also affects the intensity changes of the specular spot. Sometimes one needs sophisticated simulation using dynamical diffraction theory to interpret the phenomenon quantitatively (Ichimiya and Cohen, 2004).

The RHEED intensity oscillation is used not only for MBE growth but also in other methods of thin film growth, such as Pulsed Laser Deposition (PLD, or Laser Ablation) method for growth of oxide and nitride crystals (dielectrics, high-temperature superconductors, etc.) in the atmosphere of oxygen or nitrogen gas (Rijnders et al., 1998, 1999). In order to protect the RHEED electron gun from the high-pressure oxygen gas, differential pumping technique is employed between the growth chamber and the electron gun. The RHEED is also used for monitoring in atomic layer deposition (ALD) technique in which chemical gas phase is used for layer-by-layer growth of crystals (Tsurumi et al., 1994). The RHEED intensity oscillation is used for fabricating semiconductor superlattices with migration- enhanced epitaxy (MEE) method (Horikoshi et al., 1988). Giant magnetoresistance (GMR) and tunnel magnetoresistance multilayer structures in which a nonmagnetic atomic layer is sandwiched by magnetic layers, are fabricated by using in situ RHEED monitoring (Faure-Vincent et al., 2003).

SAMPLE PREPARATION

Samples for RHEED observation are usually prepared in situ in ultrahigh vacuum (UHV) to prevent contamination. One has to do high-temperature heating for cleaning the surface or cleavage of the crystal in vacuum to expose a flesh surface. Even slight oxidation and contamination, which make the surface region amorphous for many crystals, easily kill the RHEED patterns. Even in UHV, the beam irradiation induces accumulation of residual gases as contamination. This also degrades the quality of sample surfaces.

The sample surface should be atomically flat. As mentioned in Section "Practical Aspects of the Method", if the surface is not perfectly flat without large domains of coherent atomic arrangements, the RHEED patterns will have various modifications (see Fig. 3). Inversely, of course, such information is sometimes useful to characterize the sample surface.

PROBLEMS

In order to obtain clear and beautiful RHEED patterns, one needs a good electron beam and a good sample. In many cases in which the patterns are blurred, the electron beam is unstable and/or distorted by some reasons and/or the sample surface is not flat and/or dirty.

One of the most common reasons for the unsuccessful observations is charging-up in the apparatus. Many sample holders use insulators for electrical isolation of the sample. If the insulators are exposed so that the electron beam can "see" the insulators directly during its traveling, the beam will be distorted and deflected by charging-up of the insulators. All insulators should be hidden by metals from the electron beam along the path. The fluorescence screen as well as the sample should be conductive and grounded, otherwise they will be charged up by the electron beam irradiation. An ITO glass should be used for the screen. The acceleration voltage for the electron beam and current in electromagnets for focusing and deflection lenses should be stable, of which stability should be better than 10^{-5} . The instability of the power supplies will make ΔE and $\Delta \theta$ larger, resulting in the blurred patterns and poorer resolution in the structure determination.

If the sample surface is curved along the beam direction (as frequently occurred by high-temperature heating of samples), the glancing angle is different from place to place in the irradiated area. This results in elongation of diffraction spots perpendicular to the shadow edge. This generally cannot be distinguished from the spot elongation mentioned in Figure 3b. If the sample surface is dirty by an amorphous-like layer on it, diffraction spots are weakened with high background. If the domains/grains are small (compared with the coherence length of the beam) much like polycrystalline samples, the diffraction spots become broader and streaky (see Fig. 3). Of course, such phenomena are useful information to characterize the sample. But, very often, these cannot be distinguished from troubles in the electron beam. One may need some kind of calibration with a standard sample to ensure the apparatus working well before investigating unknown samples. A Si(111) wafer showing the (7×7) reconstructed surface shown in Figure 2b, can be a convenient standard sample if one can have ultrahigh vacuum condition and in situ heating capability up to 1500 K on the sample holder.

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