Atomic depth distribution analysis and growth dynamics of metals on metal-covered Si(111) surfaces studied by incident-angle-dependent RHEED-TRAXS (total-reflection-angle x-ray spectroscopy)

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During observation of reflection high-energy electron diffraction, characteristic x-rays are emitted from surfaces. The intensities of these x-rays change with change in the incident glancing angle ($\theta_g$) of the primary electron beam, since density distribution of electrons near the surface changes with change in $\theta_g$. By analyzing $\theta_g$ dependence of x-ray intensities, the depth distribution of elements near the surface can be determined without destruction of the surface. Resolution of depth in this method is one monolayer at the uppermost layers. By using this method, various growth motions of elements, such as substitution, alloying and floating were observed during growth of metals on metal-covered Si(111) surfaces. Morphology and growth modes of metals were significantly altered by preadsorption of other metals, and sometimes very flat metal films that would be applicable for fabrication of future electronic nano devices were obtained. In this review, the method for analysis of depth distribution of elements and growth modes of metals (Au, Ag, Ga, In and Sn) on an Si(111) surface precovered by another metal are described. [DOI: 10.1380/ejssnt.2003.91]

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I. INTRODUCTION

Growth of thin films proceeds through various elemental processes. For example, atoms or molecules that are impinged from gas phase to a surface migrate on the surface until kinetic energy dissipates into bulk. Migrating atoms or molecules find stable adsorption sites and are trapped at these sites. Sometimes preadsorbed atoms are substituted with newcomer atoms, and substituted atoms begin to migrate again. These growth motions occur not only in directions parallel to the surface but also in the perpendicular direction. Growth motions differ depending on the elements when two or more kinds of elements participate in the growth process.

There have been many reports on growth of a material on a substrate pre-covered by another element. This is because such growth processes have various potential applications to material fabrication. For example, high-quality films can be obtained by using the technique of surfactant-mediated epitaxy (SME). The use of a small amount of a surfactant element in this technique results in alternation of the growth mode from an island growth mode to a layer-by-layer growth mode. The surfactant segregates to the uppermost layer during this growth process [1-3]. Another motivation to study growth processes on pre-covered surfaces is control of the distribution of dopants in delta-doped semiconductors, since the distribution of a dopant drastically changes the electronic properties of films. Many efforts have been made to elucidate depth profiles of dopants and changes in depth profiles induced by post-annealing with a high resolution [4,5].

Growth motions of atoms in the lateral direction can be studied by using a scanning tunneling microscope on an atomic level. However, there have only been a few reports on measurements of depth distribution of elements with a resolution close to one monolayer [6,7]. It is much more difficult to determine how elements move during growth in the perpendicular direction with a monolayer resolution.

The author developed a method to analyze depth distribution of elements with a high resolution close to one monolayer without destruction of grown films [8,9]. In this method, intensity of characteristic x-rays emission, which is induced by an electron beam of reflection high-energy electron diffraction, is measured as a function of glancing angle ($\theta_g$) of the primary beam (See Fig. 1.). By analyzing depth distribution of elements step by step after each monolayer deposition, it is possible to observe the growth motion of each element in the direction perpendicular to the surface during the growth process. In this review, the principle of the method for analysis of depth distribution of elements is first described. Then growth modes of metals on Si(111) surfaces that were each pre-covered by another metals, which were determined by using this method, will be described. Various growth motions of elements, including substitution, alloying and segregation to the uppermost layer, many of which are difficult to observe by using other techniques, were observed by using the method developed by the author.

II. PRINCIPLE OF THE METHOD

A. Outline

When an electron beam is incident on a surface, the direction of electron trajectories deviates from the initial direction and the energy of electrons gradually decreases through repetition of elastic and inelastic scattering processes. As a result, the distribution of electron trajectories becomes a droplet-like shape. The depth distribution of the trajectories changes with change in $\theta_g$. For example, electron trajectories segregate to surface layers at low $\theta_g$, while trajectories reach deeper regions at high $\theta_g$. Therefore, X-ray emission from a specific layer also changes with change in $\theta_g$ depending on the depth of the layer. Thus, depth of elements can be analyzed from $\theta_g$ dependence

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of x-ray intensity. The experimental results are analyzed by calculation of electron trajectories based on results of Monte Carlo simulation.

B. Detail of calculation

Electron trajectories have often been calculated by Monte Carlo simulation to explain various phenomena related to electron beams impinging into solid materials [10-18]. In this simulation, various scattering processes can be treated flexibly, and many phenomena in electron probe microanalysis (EPMA) and scanning electron microscopy (SEM), e.g., normal incidence of high-energy electrons, have been successfully reproduced [10-18]. The author has shown that the Monte Carlo method is also very useful for understanding electron trajectories in RHEED.

Advanced Monte Carlo simulation applied for calculation of secondary and Auger electrons, and characteristic X-ray emissions has been reviewed in detail by Shimizu [10]. However, we used a simplified method in which the interaction between incident electrons and a solid is divided into elastic and inelastic scattering processes [9, 11]. In elastic scattering, electrons are scattered by Coulomb potential of individual atomic cores, and only the direction is changed without loss of kinetic energy. In the inelastic scattering process, the kinetic energy of electrons gradually dissipates without changing directions of their propagation.

The following equations are used in this method. The Rutherford differential cross section, $dQ(\theta)$, for elastic scattering of an electron by an atom is given by

$$dQ(\theta) = \frac{e^4 Z^2}{16(4\pi\epsilon_0 E)^2} \frac{d\Omega}{\sin^2(\theta/2) + (\theta_0^2/4)^2},$$

where $\theta$ is the scattering angle, $E$ is the electron energy, $d\Omega = 2\pi \sin \theta d\theta$ is the element of the solid angle into which the electron is scattered at an angle $\theta$ from its incident direction, $e$ is the electronic charge, $Z$ is the atomic number of the scattering atom, $\epsilon_0$ is the dielectric constant,

and $\theta_0^2/4$ is the screening parameter, $\delta$, and is numerically equal to

$$\delta = \frac{\theta_0^2}{4} = 3.4 \times 10^{-3} \frac{Z^{2/3}}{E},$$

where $E$ is in keV. The angular deviation of the trajectory caused by inelastic scattering is negligible. The mean free path $\lambda$ of an electron in a solid is given by

$$\lambda = \frac{A}{QN_0 \rho} \text{ (cm/event)},$$

where $N_0$ is Avogadro’s number, $A$ is the atomic weight, and $\rho$ is the density. The energy loss rate due to all of the inelastic scattering processes was estimated by Bethe. The energy loss $dE$ per unit of distance $dx$ traveled in a
solid is given by
\[
dE/dx = -\frac{2\pi e^4 N_0 Z \rho}{AE_m} \cdot \log(1.166 E_m/J)
\]
\[= -7.85 \times 10^4 \cdot \frac{Z \rho}{AE_m} \cdot \log(1.166 E_m/J)\ (keV/cm),
\]
where \(E_m\) is the mean energy across the distance interval \(dx\), and \(J\) is the mean ionization potential, which is the average energy loss per interaction considering all possible energy loss processes. \(J\) is defined as
\[
J = (9.76Z + 58.5Z^{-0.19}) \times 10^{-3}\ (keV).
\]
The cross section for inner shell ionization, \(Q_i\), is given by
\[
Q_i E_i^2 = 5.52 \times 10^{-14} Z \ln \frac{U}{U + 1.32},
\]
where \(U = E/E_i\) (\(E_i\) is the ionization energy of the inner shell) \[19\].

Using the above equations, the trajectories of the electrons and X-ray emission intensity can be obtained by repeating processes (i)-(iv).

(i) The electron (energy=\(E\)) travels straight in a direction \(D\), from a starting point \(P\), to the first elastic scattering point \(P'\), which is at a distance \(l\) from the starting point \(P\) set by \(l = -\lambda \ln R\), where \(R\) is a random number (0 < \(R\) < 1).

(ii) The rate of X-ray emission from a specific region is assumed to be proportional to \(LQ_i\), where \(L\) is the electron path length in the region.

(iii) A new energy \(E'\) is obtained from Eq. (3), and a new direction of the electron \(D'\) and a new mean free path \(\lambda'\) are obtained from Eqs. (1) and (2), respectively, using the new energy \(E'\).

(iv) The electron travels in the new direction \(D'\) to the next elastic scattering point \(P''\), which is at a distance \(l''\) set by \(l'' = -\lambda' \ln R\) from \(P''\).

In the most advanced method, the scattering cross section is given by solution of the relativistic Dirac equation using the Thomas-Fermi-Dirac atomic potential \[10\].

C. \(\theta_g\) dependence of X-ray emission and analysis of atomic depth distribution

By applying the above Monte Carlo simulation, electron trajectories and X-ray emission yields under the condition of RHEED were calculated. By studying X-ray emissions at various depth regions and at various values of \(\theta_g\) \[9\], it was found that \(\theta_g\) dependences of X-ray emission differ depending on the depth of atoms emitting X-rays. Figure 2 shows results of Monte Carlo electron trajectory simulation for 10 monolayers (MLs) of Ag on Si. The number of incident electrons is 100 and the incident electron energy...
FIG. 5: Growth modes of metals (metals B) on Si(111) surfaces pre-covered by one monolayer of other metals (metals A) determined by the present method. (a) Metal B grows on a layer of metal A (Ag/$\sqrt{3} \times \sqrt{3}$-Au and In/6.3 $\times$ 6.3-Ga). (b) Metal A segregates to the uppermost layer (Au/$\sqrt{3} \times \sqrt{3}$-Ag and Ga/4 $\times$ 1-In). (c) Intermixing between metals A and B occurs after deposition of 1 ML of metal B. During further deposition of metal B, metal A segregates to the uppermost layers (Ag/$\sqrt{3} \times \sqrt{3}$-Ga(1ML) and Au/$\sqrt{3} \times \sqrt{3}$-Ga(1 ML)). (d) Intermixing between metals A and B occurs after deposition of 1 ML of metal B. During further deposition of metal B, segregation of a part of metal A and intermixing of the other part of metal A with metal B occur (Ag/4 $\times$ 1-In and Au/2$\sqrt{3} \times 2\sqrt{3}$-Sn). (e) Intermixing between metals A and B always occurs (Ag/2$\sqrt{3} \times 2\sqrt{3}$-Sn and Ga/2$\sqrt{3} \times 2\sqrt{3}$-Sn). (f) Metal B first grows on a layer of metal A but intermixing between metals A and B occurs above a critical coverage of metal B (Ga/4$\sqrt{3} \times \sqrt{3}$-Au). (g) After deposition of 1 ML of metal B, substitution between metal A and metal B occurs, resulting in the formation of islands of metal A on a layer of metal B. During further deposition of metal B, metal B grows surrounding metal A (Ga/$\sqrt{3} \times \sqrt{3}$-Ag). (h) About 2 ML of metal B grows on a layer of metal A. During further deposition of metal B, metal A always segregates to the third layer (In/$\sqrt{3} \times \sqrt{3}$-Ga(1 ML)). (i) Intermixing between metal A and metal B occurs after deposition of 1 ML of metal B. During further deposition of metal B, metal B grows into islands on layers of A-B alloy (Sn/$\sqrt{3} \times \sqrt{3}$-Ga(1 ML)).

is 10 keV. Figs. 2a-2c correspond to the incident glancing angles of 0.5°, 10° and 25°, respectively, and the scale of depth is five-times greater than that in the direction parallel to the surface. In the first layer, A, in Fig. 2a, the total length of the trajectories is very large, resulting in increased X-ray emission. At higher $\theta_g$, the total length became smaller as seen in Figs. 2b and 2c. On the other hand, only 42 of the 100 incident electrons could reach layer B at $\theta_g$=0.5°, as seen in Fig. 2a, and the X-ray emission decreased markedly. When $\theta_g$ was increased to 10°, 84 electrons were impinged in layer B, as shown in Fig. 2b, and 94 electrons reached layer B at $\theta_g$ =25°, as shown in Fig. 2c. By studying the lengths of trajectories at various depths and various $\theta_g$, $\theta_g$ dependences of the X-ray emissions from thin regions of various depths were obtained as shown in Fig. 3. It is seen that $\theta_g$ dependences of x-ray emission from various layers change depending on their depth. The peak position shifts to a higher angle as depth increases. Thus, the depths of specific elements can be determined by measuring $\theta_g$ dependence of the characteristic X-ray emission.
III. APPARATUS

Generally, characteristic x-ray spectroscopy is not surface-sensitive because the escape depth of x-rays is several micrometers. However, it becomes surface-sensitive by placing the x-ray take-off angle (θt) at a grazing angle close to the critical angle for total reflection [20-26] as shown in Fig. 1, a technique known as total reflection angle x-ray spectroscopy (RHEED-TRAXS) [25]. This method was used in the present study. However, accurate measurement of θg dependences still have the following difficulties.

(1) Under the TRAXS condition, x-ray yields change sensitively with very small changes in θt. To eliminate this effect, it is desirable that the sample and detector are fixed during scanning of θt.

(2) The beam size should be small and the area of the surface relative to the beam size should be very large so that the entire beam falls on the surface at low θg, because information on surface structure is derived mainly from the low angle part (θg < 5°) of θg dependences.

(3) Very flat surfaces over a wide area are required so that θt is constant when the position of the irradiated area shifts on the surface during scanning of θg, because under the TRAXS condition, the x-ray yields change greatly with only small changes in θt, as mentioned above.

Figure 4 shows a schematic illustration of the apparatus [27]. A small electron gun is rotated in ultra-high vacuum (UHV) around the sample, and the sample and detector are fixed during scanning of θg. Special care was taken to make wide flat surfaces and a small electron beam. A turntable with a large gear was mounted on stainless steel bearings fixed at the center of the chamber, and a small electron gun was placed on the table. A sample was placed on the rotation axis of the turntable, and θg was scanned by rotating the turntable with the electron gun. The table was rotated by transmitting the motion of a stepping motor outside the chamber via a small gear in vacuum. The x-rays emitted from the sample surface during irradiation of an electron beam took off into the air through a Be window that was placed on the axis of rotation, and they were detected by a solid state detector (SSD). To reduce beam size in the vertical direction, a slit was made in the front of the gun. The slit was made using two Ta sheets, and the width of the slit is 0.1 mm. An Si(111) sample of 12 mm in diameter and 0.5 mm in thickness was cut from an Si wafer polished to a mirror finish and mounted on a holder that can rotate around a fulcrum, and θt was optimized by tilting the stage to move the SSD and the slit up and down. The tilt of the stage was controlled by a micrometer and a stepping motor.

IV. ATOMIC DEPTH DISTRIBUTION AND GROWTH MODES OF METALS ON Si(111) SURFACES PRECOVERED BY OTHER METALS

Controlling growth of metal thin films on Si surfaces is important for fabrication of good metal-semiconductor interfaces. In this section, growth modes of metals on Si(111) surfaces each pre-covered by another metal, which were studied by the above-described method, are summarized. Ag, Au, Ga, In and Sn were grown on Si(111)-α-√3×√3-Au. [from Ref.9]. (b) Ag(15 ML)/Si(111)-√3×√3-Ga(1 ML). (c) Ag(6 ML)/Si(111)-4×1-In. (d) Ag(5 ML)/Si(111)-2√3×2√3-Sn. [from Ref. 32]. Spots in (a) indicate formation of Ag particles. (b), (c) and (d) show streaks indicating that grown films are flat. However, features of patterns in (b), (c) and (d) are different indicating that grown films have different structures. For example, inclined curves indicated by an arrow in (c) suggest an anisotropic structure of the film in a plane parallel to the surface, while such curves are not seen in (b) and (d). (d) shows wide parabolic lines indicated by a dashed line suggesting the formation of a flat surface that consists of heavy atoms.

A. Growth of Ag

It is well known that Ag is adsorbed at the initial stage of growth of Ag on an Si(111)-7 × 7 surface at room temperature, resulting in the formation of clusters at the faulted part of 7 × 7 unit cells [28, 29] and that larger islands are formed at higher coverages of Ag [30, 31]. The formation of islands is clearly indicated by transmitted spots in RHEED patterns [30, 31].
FIG. 7: $\theta_g$ dependencies of intensity of characteristic x-rays emitted from surfaces during growth of Ag on Si(111)-$\sqrt{3} \times \sqrt{3}$-Au [from Ref. 9] and $\sqrt{3} \times \sqrt{3}$-Ga(1 ML) surfaces. [from Ref. 32].

(a) Ag(1 ML)/Si(111)-$\sqrt{3} \times \sqrt{3}$-Au. (b) Ag(8 ML)/Si(111)-$\sqrt{3} \times \sqrt{3}$-Au. (c) Ag(1 ML)/Si(111)-$\sqrt{3} \times \sqrt{3}$-Ga(1 ML). (d) Ag(15 ML)/Si(111)-$\sqrt{3} \times \sqrt{3}$-Ga (1 ML).

A RHEED pattern obtained during growth of Ag on an Si(111)-$\sqrt{3} \times \sqrt{3}$-Au surface is similar to that for growth of Ag on an Si(111)-7 $\times$ 7 surface, as shown in Fig. 6a (Coverage of Ag is 1 monolayer (ML) ($\Theta_{Ag} = 1$.) [9]. It was clearly shown that Ag grows on an Au layer. $\theta_g$ dependences of characteristic x-rays, SiK, AgL and AuM, taken during this growth process are shown in Figs. 7a and 7b. Since the diameters of the incident electron beam and the sample were about 0.15 mm and 12 mm, respectively, the entire beam fell on the sample at $\theta_g$ above 0.7°. The rapid decreases in x-ray yields below 0.7° are due to the finite size of the sample. At Ag coverage of 1 ML ($\Theta_{Ag} = 1$), $\theta_g$ dependences of AgL had maxima at 1° and decreased above $\theta_g$ = 1° with increases in $\theta_g$, as shown in Fig. 7a. On the other hand, the intensity of AuM showed a maximum at 2.5° and that of SiK had a broad maximum at 14°. Based on a comparison of these results with the calculated $\theta_g$ dependencies shown in Fig. 3, it is concluded that one monolayer of Ag grew on an Au layer. After 8 ML of Ag deposition, the maxima of AuM and AgL intensities shifted to higher angles of 3° and 9°, respectively, indicating that 8 ML of Ag existed on the preadsorbed Au layer (ordinary growth mode), as shown in Fig. 5a. Although occurrence of this growth mode seems very natural, this growth mode was rarely observed in the other growth processes of Ag, Au, Ga, In and Sn studied by the present method. It is thought that the origin of occurrence of the ordinary growth mode of Ag on Au/Si is related to the strong binding of Au to the Si surface.

In contrast to the growth of Ag on an Si(111)-$\sqrt{3} \times \sqrt{3}$-Au surface, the morphology of Ag films was
altered when $\sqrt{3} \times \sqrt{3}$-Ga(1ML), $4 \times 1$-In and $2\sqrt{3} \times 2\sqrt{3}$-Sn structures were prepared prior to Ag growth by deposition of one monolayer of Ga, In, and Sn, respectively [32]. RHEED patterns taken during these growth processes all showed streaks, indicating formation of flat Ag films. Based on results of analysis of depth distribution of elements, growth modes shown in Figs. 5c (Ag/Ga) and 5e (Ag/Sn) were concluded. In these growth processes, preadsorbed atoms are thought to act as surfactants. Figures 7c and 7d show $\theta_g$ dependencies after deposition of 1 ML and 15 MLs of Ag on an Si(111)-$\sqrt{3} \times \sqrt{3}$-Ga(1ML) surface that was made by deposition at room temperature of an additional 2/3 ML of Ga on an Si(111)-$\sqrt{3} \times \sqrt{3}$-Ga(1/3 ML) surface. In Fig. 7c, the behaviors of AgL and GaK are very similar, indicating intermixing between Ag and Ga. On the other hand, the angle of maximum of AgL is lower than that of GaK in Fig. 7d, indicating segregation of Ag atoms to the uppermost layers. These results were explained well by results of calculation assuming the growth mode in Fig. 5c as shown by solid and dashed lines in Fig. 7d. Details of calculation are given in ref. [32].

**B. Growth of Au**

Growth of Au on an Si(111)-7 $\times$ 7 surface has been extensively studied. During growth of Au on an Si(111)-7 $\times$ 7 surface, formation of particles was observed around $\Theta_{Au} = 3$ in an STM study [33], and RHEED patterns during this growth showed weak transmitted spots characteristic of particles [34]. However, at high $\Theta_{Au}$, some Si atoms segregate to the uppermost layers, resulting in the formation of Au-Si silicide layers [35], and the resultant Au film is flat [36]. Thus, floating Si may act as a surfactant at high $\Theta_{Au}$, and flat films can be obtained without preadsorption of another element. However, Au films at low $\Theta_{Au}$ were further altered to flatter films by preadsorption of metals. During growth of Au on $\sqrt{3} \times \sqrt{3}$-Ga(1ML), $4 \times 1$-In and $2\sqrt{3} \times 2\sqrt{3}$-Sn surfaces, RHEED patterns showed streaks indicating the formation of flat films even at low $\Theta_{Au}$ [32]. Considering $\theta_g$ dependencies of x-ray emission, growth modes in Figs. 5c (Au/Ga) and 5d (Au/In and Au/Sn) were concluded. These results indicate that the surfactant effects of Ga, In and Sn are also significant. The possibility of the existence of surface silicide layers could not be ruled out by analysis of RHEED patterns and $\theta_g$ dependencies, and Si may also exist in the uppermost layers at high $\Theta_{Au}$ [37].

During growth of Au on $\sqrt{3} \times \sqrt{3}$-Ag, surface segregation of Ag and formation of flat Au films were also observed [9]. However, during this growth, Ag atoms on the Au films grow into particles, and the sizes of islands become larger with increase in $\Theta_{Au}$ [37].

During growth of Au on all the above four metal-covered surfaces, substitution between pre-adsorbed atoms and Au always occurred. This is consistent with strong binding of Au to Si surfaces.

**C. Growth of Ga**

Growth of Ga has not been studied extensively on an atomic scale because Ga is liquid with a melting point of 30$^\circ$C. However, Ga is a key material in semiconductor technology related to GaAs and GaN, and controlling the growth mode of Ga on a semiconductor is very important. For example, Ga grows into droplets of uniform sizes on a semiconductor surface. By exposure of these droplets to As$_2$ or NH$_3$, it is possible to fabricate quantum dots of GaAs and GaN of uniform sizes, a technique known as droplet epitaxy [38-41]. It is naturally expected that morphology of GaAs and GaN films can be designed by controlling the growth of Ga. Actually, many new growth modes were observed during growth of Ga on Si(111)-2$\sqrt{3} \times 2\sqrt{3}$-Sn, 4 $\times$ 1-In, $\sqrt{3} \times \sqrt{3}$-Ag and $\alpha-\sqrt{3} \times 2\sqrt{3}$-Au surfaces.

A clear alloying between Ga and preadsorbed Sn was observed during growth of Ga on an Si(111)-2$\sqrt{3} \times 2\sqrt{3}$-Sn surface [42]. Fig. 8a shows a RHEED pattern obtained after deposition of 1 ML of Ga on an Si(111)-2$\sqrt{3} \times 2\sqrt{3}$-Sn surface. This pattern indicates that the surface is flat. $\theta_g$ dependencies of GaK and SnL obtained from this surface are very similar, as shown in Fig. 9a. These results indicate that Ga and Sn are mixed with each other, resulting in the formation of a flat film. However, after deposition of 7 ML of Ga, the RHEED showed halo rings indicating that the grown film is liquid, as shown in Fig. 8b. $\theta_g$ dependencies of GaK and SnL are still very similar (Fig. 9b). Therefore, a liquid Sn:Ga alloy formed on the surface, as shown by the growth model in Fig. 5e (alloying growth mode). This growth mode does not contradict the bulk phase diagram showing that 7 ML of Ga and 1 ML of Sn can mix as a liquid phase above 40$^\circ$C although the present experiment was conducted at room temperature [43].

Alloying of Ga with preadsorbed Au was observed also in the growth of Ga on an Si(111)-$\alpha-\sqrt{3} \times 2\sqrt{3}$-Au surface. However, in this growth process, it was found that there is a critical Ga coverage of about 1 ML above which dissociation of Au and formation of an Au-Ga alloy start [44]. Figure 10a shows a RHEED pattern of an Si(111)-$\alpha-\sqrt{3} \times \sqrt{3}$-Au surface. After deposition of 1 ML of Ga on this surface ($\Theta_{Ga}=1$), the RHEED pattern still showed $\sqrt{3} \times \sqrt{3}$ spots/streaks indicating a flat surface, but the intensity distribution in the pattern changed, as is shown in Fig. 10b ($\theta_g=2.7^\circ$). Figure 11a shows $\theta_g$ dependen-
FIG. 9: $\theta_g$ dependencies of intensity of characteristic x-rays emitted from surfaces during growth of Ga on an Si(111)-2$\sqrt{3}$ × 2$\sqrt{3}$-Sn. (a) Ga(1 ML)/Si(111)-2$\sqrt{3}$ × 2$\sqrt{3}$-Sn. (b) Ga(7 ML)/Si(111)-2$\sqrt{3}$ × 2$\sqrt{3}$-Sn. [from Ref. 42].

FIG. 10: RHEED patterns taken during deposition of Ga on an Si(111)-$\alpha$-$\sqrt{3}$ × $\sqrt{3}$-Au surface at room temperature. (a) Si(111)-$\alpha$-$\sqrt{3}$ × $\sqrt{3}$-Au. $\theta_g=2.5^\circ$ (b) $\Theta_{Ga}=1$ and $\theta_g=2.5^\circ$. (c) $\Theta_{Ga}=2$ and $\theta_g=0.5^\circ$. [from Ref. 44].

cies of GaK, AuM and SiK characteristic x-ray emissions taken from this surface. These results indicate that Ga atoms exist in the uppermost layer and that Au atoms exist in the second layer, conserving the $\sqrt{3}$ × $\sqrt{3}$ periodicity. However, alloying between Ga and Au occurred above $\Theta_{Ga}=1$. During further deposition of Ga, a RHEED pattern showed transmitted spots of AuGa$_2$ as shown in Fig. 10c. Weak rings of halo patterns, suggesting the existence of excess liquid Ga, were also seen at high $\Theta_{Ga}$. Figures 11b and 11c show $\theta_g$ dependencies taken at $\Theta_{Ga}=2$ and $\Theta_{Ga}=5$, respectively. The dashed lines shows calculated $\theta_g$ dependence of AuM assuming that Ga exists on an Au layer without intermixing, and this curve significantly deviates from the experimental results. This indicates that significant alloying between Ga and Au occurred. The solid lines in Fig. 11c show simulation of AuM and GaK curves assuming that Au and Ga are mixed but that the concentration of Ga in the 1st and 2nd layers is 1.2-times higher than that in the 3rd to 6th layers. These curves can explain the experimental results. However, such analysis shows only qualitative atomic depth distribution and the degree of intermixing, since a flat film is assumed in the calculation despite the fact that there were islands on the surface. Based on the results of RHEED observation and analyses of atomic depth distribution, a growth model of Ga on an Si(111)-$\alpha$-$\sqrt{3}$ × $\sqrt{3}$-Au surface is proposed as shown in Fig. 5f. It is thought that the critical coverage for alloying between Au and Ga is related to stoichiometry of the resultant alloy. In a previous study using a Ga/Sn/Si system, the resultant Ga-Sn alloy was liquid, and its atomic structure and composition ratio of Ga to Sn were therefore rather flexible, and thus alloying between Ga and Sn was always observed from low $\Theta_{Ga}$ to high $\Theta_{Ga}$. On the other hand, in the Ga/Au/Si system, the resultant alloy has a well-ordered structure of an AuGa$_2$ crystal, and eight Ga atoms are needed to form one unit cell of AuGa$_2$. Thus, some critical local Ga coverage may be required to supply a sufficient number of Ga atoms for alloying.

A more complex growth motion was observed during growth of Ga on Si(111)-$\sqrt{3}$ × $\sqrt{3}$-Ag [42]. Considering results of RHEED observation and depth distribution analysis, a growth mode in Fig. 5g was concluded. In this growth, after deposition of 1 ML of Ga, Ag atoms were substituted with Ga atoms, resulting in the formation of Ag particles on an underlying Ga layer. During further deposition of Ga, Ga grew surrounding the Ag particles. The growth behavior of this process was confirmed by local elementary analysis using ultra-high vacuum scanning electron microscopy with TRAXS [45].

In the above three growth processes, Ga always grew into liquid droplets at higher coverages. However, it was found that Ga grows into flat ordered films on an Si(111)-4 × 1-In surface [46]. During this growth process, a RHEED pattern at low $\theta_g$, which contains information...
on shallow regions, showed streaks corresponding to a $\sqrt{3}/2 \times \sqrt{3}/2$ periodicity, indicating formation of a flat film, as shown in Fig. 12a. On the other hand, a RHEED pattern at high $\theta_g$, which contains information on structure in deeper regions, showed spots corresponding to a $5 \times 5$ periodicity (Fig. 12b). Therefore, the grown film has $\sqrt{3}/2 \times \sqrt{3}/2$ and $5 \times 5$ periodicities at the surface and the Si-Ga interface, respectively.

D. Growth of In

As well as Ga, In is also an important material in the growth of compound semiconductors such as InAs and InSb. By applying the technique of droplet epitaxy, quantum dots of InAs with uniform sizes have been fabricated [47]. It may be possible to grow flat films of InAs and InSb on Si substrates if flat In films are obtained on Si substrates. Actually, it was found that In grows into atomically flat films on Si(111)-$\sqrt{3} \times \sqrt{3}$-Ga(1 ML) [48-50]. During this growth process, it was also found that Ga always segregates to the third layer acting as a surfactant, as shown in Fig. 5h. The grown film was atomically flat as shown by observation by an ultra-high vacuum scanning electron microscope (Fig. 14) [49,50]. A RHEED pattern obtained during this growth showed streaks corresponding to a $\sqrt{3}/2 \times \sqrt{3}/2$ periodicity at low $\theta_g$. On the other hand, a RHEED pattern obtained at high $\theta_g$ showed spots corresponding to a $\sqrt{3} \times \sqrt{3}$ periodicity. Therefore, the grown film has $\sqrt{3}/2 \times \sqrt{3}/2$ and $\sqrt{3} \times \sqrt{3}$ periodicities at the surface and the Si-metal interface, respectively.

The author studied the growth of In on an Si(111)-$6.3 \times 6.3$-In surface that was prepared by deposition of 1 ML of Ga on a $7 \times 7$ clean surface at 500°C and the growth of In on a surface that was prepared by deposition of 1 ML of Ga onto a $7 \times 7$ clean surface at room temperature [48]. In both cases, In grew into islands on Ga layers, indicating that initial structure of a metal-covered surface affects the growth mode of a post grown metal.
E. Growth of Sn

There have been many studies on the growth processes of Sn on semiconductor surfaces. One of motivations for these works is the potential applications of Sn films to fabrication of infrared electronic devices, since Sn is a semiconductor with a very narrow bandgap at temperatures below 13 °C. It was found that this semiconductor phase of Sn was stable even at higher temperatures (<170 °C) when Sn was epitaxially grown on an InSb(111) surface [51]. Co-adsorption of Sn and other elements on semiconductor surfaces has also been studied because preadsorbed Sn acts as a surfactant during growth of semiconductors [52] and metals [32]. However, there have been only a few reports in which the growth process of Sn on a semiconductor surface precovered by another element is described.

During growth of Sn on an Si(111)-7 × 7 surface, the formation of Sn islands has been observed at small Sn coverages below $\Theta_{Sn} = 1$ [53-55]. However, in the growth of Sn on an Si(111)−$\sqrt{3} \times \sqrt{3}$-Ga(1 ML) surface, a flat film of Ga-Sn alloy was formed at $\Theta_{Sn} \leq 1$. During further deposition of Sn, Sn then grew into islands on the layers of Ga-Sn alloy, as shown in Fig. 5i. In this growth process, the surfactant effect of Ga was limited to coverages of $\Theta_{Sn} \leq 1$.

In the growth of Sn on Si(111)-α-\(\sqrt{3} \times \sqrt{3}\)-Au and 4 x 1-In surfaces, alloying occurred between Sn and Au, and between Sn and In, respectively [56]. The grown films consisted of islands of these alloys. At present it seems difficult to grow flat Sn films on Si(111) surfaces.

V. CONCLUDING REMARKS

By analyzing $\theta_g$ dependences of characteristic x-rays, it is possible to determine the depth distribution of elements near the surface. The resolution of depth is about one monolayer in shallow regions, and destruction of surfaces during these measurements is thought to be negligibly small in many cases. Thus, the motion of elements and their timing during growth processes can also be determined by analyzing the distribution of elements when coverages of grown atoms are changed step by step. By using this method, various growth modes of metals on Si(111) surfaces precovered by other metals have been discovered. Analysis of the depth distribution of elements is difficult by using other methods. This method can be applied qualitatively even when the surface contains islands. In such cases, however, quantitative analysis of depth distribution requires more detailed Monte Carlo simulation that can treat islands of various sizes and shapes. By using a scanning tunneling microscope or an ultra-high-vacuum scanning electron microscope together with the present method, it is possible to determine growth motion of elements in three-dimensional space. Such study is important for the control of growth of materials and for the design of new nano structures.

Other than our works, surfactant growth has been extensively studied only for growth of semiconductors on semiconductors and metals on metals. Results of our works suggest that a high-quality layer-by-layer growth
mode of a metal on an Si surface is a rare phenomenon. However, it was found that Ga and In grew into very flat films by using In and Ga, respectively, as surfactants. Since these metals are key materials in the growth of compound semiconductors, such growth processes may become important for the fabrication of new electronic devices.

[1] M. Copel, M. C. Reuter, E. Kaxiras and R. M. Tromp, Phys. Rev. Lett. 63, 632 (1989).
[2] M. Horn-von Hoegen, F. K. LeGoues, M. Copel, M. C. Reuter and R. M. Tromp, Phys. Rev. Lett. 67, 1130 (1991).
[3] H. A. van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg and J. M. C. Thornton, Phys. Rev. Lett. 68, 3335 (1992).
[4] T. Kobayashi, C. F. McClonville, G. Dorenbos, M. Iwaki and M. Aono, Appl. Phys. Lett. 74, 673 (1999).
[5] V. V. Chaldyshev, N. A. Bert, Yu. G. Musikhin, A. A. Suvorova, V. V. Preobrazhenskii, M. A. Putyato, B. R. Semyagin, P. Werner and U. Göhrsele, Appl. Phys. Lett. 79, 1294 (2001).
[6] K. Nakajima, A. Konishi and K. Kimura, Phys. Rev. Lett. 83, 3802 (1999).
[7] J. Steinshneider, J. Harper, M. Weimer, C.-H. Lin, S. S. Pei and D. H. Chow, Phys. Rev. Lett. 85, 4562 (2000).
[8] T. Yamanaka, T. Hanada, S. Ino and H. Daimon, Jpn. J. Appl. Phys. 31, L1503 (1992).
[9] T. Yamanaka, A. Endo and S. Ino, Surf. Sci. 294, 53 (1993).
[10] R. Shimizu, Jpn. J. Appl. Phys. 22, 1631 (1983).
[11] D. E. Newbury, in Advanced Scanning Electron Microscopy and X-ray Microanalysis, eds. D. E. Newbury, D. C. Joy, P. Echlin, C. E. Fiori and J. I. Goldstein (Plenum Publishing Corporation, New York, 1986) p. 3.
[12] K. Murata, T. Matsukawa and R. Shimizu, Jpn. J. Appl. Phys. 10, 678 (1971).
[13] R. Shimizu and K. Murata, J. Appl. Phys. 42, 387 (1971).
[14] S. Ichimura and R. Shimizu, Surf. Sci. 112, 386 (1981).
[15] H. E. Bishop, Phys. Rev. Lett. 42, 196101 (1999).
[16] V. L. Reimer, H. Gilke and K. H. Sommer, Optik 30, 590 (1970).
[17] V. L. Reimer, Optik 27, 86 (1968).
[18] H. E. Bishop, Brit. J. Appl. Phys. ser. 2, 1, 673 (1968).
[19] C. J. Powell, NBS Spec. Pub. p.97 (1976).
[20] P. B. Swell and M. Cohen, Appl. Phys. Lett. 11, 298 (1967).
[21] P. B. Swell and D. F. Mitchell, J. Appl. Phys. 42, 5879 (1971).
[22] D. F. Mitchell, P. B. Swell, and M. Cohen, Surf. Sci. 61, 335, (1976).
[23] S. Ino, T. Ichikawa and S. Okada, Jpn. J. Appl. Phys. 19, 1451 (1980).
[24] R. S. Becker J. A. Golovchenko and J. R. Patel, Phys. Rev. Lett. 50, 153 (1982).
[25] S. Hasegawa, S. Ino, Y. Yamamoto and H. Daimon, Jpn. J. Appl. Phys. 24, L387 (1985).
[26] S. Hasegawa, H. Daimon and S. Ino, Surf. Sci. 186, 138 (1987).
[27] T. Yamanaka and S. Ino, Rev. Sci. Inst. 72, 1477 (2001).