

Transition from Overlayer Growth to Alloying Growth of Ga on Si(111)- α - $(\sqrt{3} \times \sqrt{3})$ -Au

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Atomic depth distribution and growth modes of Ga on an Si(111)- α - $(\sqrt{3} \times \sqrt{3})$ -Au surface at room temperature were studied after each monolayer deposition of Ga via reflection high-energy electron diffraction and characteristic x-ray spectroscopy measurements as functions of glancing angle θ_g of the incident electron beam. One monolayer of Ga grew on the Au layer, and the $\sqrt{3} \times \sqrt{3}$ periodicity was conserved below the Ga overlayer. Above a critical Ga coverage of about one monolayer, this growth mode drastically changed; i.e., Au atoms dissociated from the $\sqrt{3} \times \sqrt{3}$ structure and Ga grew into islands of Ga-Au alloy.

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Growth of thin films proceeds through various processes such as diffusion, nucleation, and substitution, and such growth motions in both lateral and perpendicular directions differ depending on elements when the growth system contains two or more elements. There have been many reports on growth of a material on a substrate precovered by another element, since such growth processes have various potential applications to material fabrication. A typical example is surfactant-mediated epitaxy (SME) in which a small amount of a surfactant element alters the growth mode from an island growth mode to a layer-by-layer growth mode, and the surfactant segregates to the uppermost layer during this growth [1–3]. This technique is useful for fabrication of high-quality films. Another motivation to study growth processes on precovered surfaces is control of the distribution of dopants in delta-doped semiconductors. The distribution of a dopant significantly affects the electronic properties, and many efforts have made to obtain high-resolution depth profiles of dopants and changes of depth profiles induced by postannealing [4,5].

Although growth motions of atoms in the lateral direction can be studied by using a scanning tunneling microscope on an atomic level, there have been only a few reports on measurements of depth distribution of elements with a resolution close to a monolayer [6,7]. It is still difficult to determine how elements move during growth in the perpendicular direction with monolayer resolution. The timing of movement of atoms during growth is also an important issue, but there are also very few reports on *in situ* observation of perpendicular motions of atoms during growth. Elucidation of these issues requires determination of the distribution of elements with high depth resolution and without destruction of samples, changing coverages of grown atoms in detail.

In this paper, the growth of Ga on an Si(111)- α - $(\sqrt{3} \times \sqrt{3})$ -Au surface at room temperature is described. Atomic depth distribution was analyzed with resolution of about a

single monolayer at various coverage of Ga, and a new transition of growth mode was found. After 1 ML of Ga deposition, Ga grew into an overlayer on the Au layer, and the α - $\sqrt{3} \times \sqrt{3}$ -Au structure was conserved below the Ga overlayer. However, during further deposition of Ga, Au dissociated from the $\sqrt{3} \times \sqrt{3}$ -Au structure and alloying between Ga and Au occurred. Therefore, there is a critical Ga coverage of about one monolayer (ML) above which dissociation of Au and formation of an Au-Ga alloy start, and this critical coverage and a transition of growth mode were directly observed by high-resolution atomic depth resolution analysis.

In this work, morphology of grown films was analyzed by reflection high-energy electron diffraction (RHEED), and atomic depth distribution was analyzed from characteristic x-ray intensity excited by a RHEED beam as a function of incident glancing angle, θ_g [8]. By this method, a resolution of one monolayer for the uppermost layers and a resolution of a few monolayers for deeper layers were achieved. For sensitive detection of x rays from surfaces, we used a technique called total reflection angle x-ray spectroscopy (TRAXS) [9,10], in which the x-ray detector is placed at an angle near the critical angle for total reflection. The apparatus used has been described in detail in a previous paper [11]. The electron gun was operated at an acceleration voltage of 15 keV. The x rays were detected by an Si(Li) detector. Cleaning of the Si(111) surface was performed by heating above 1200 °C by electron bombardment until a clear 7×7 RHEED pattern was observed. An Si(111)- α - $(\sqrt{3} \times \sqrt{3})$ -Au surface was prepared by deposition of 2/3 monolayer (ML) of Au onto the 7×7 surface at 500 °C [12] from coiled tungsten filaments. This surface was cooled to room temperature, and Ga was then deposited from another filament.

The principle of the method for analysis of atomic depth distribution is as follows. During irradiation of an electron beam on a solid surface, the distribution of

electron trajectories in the solid drastically changes depending on θ_g . At small θ_g , the trajectories localize near the uppermost layer, but the trajectories reach deeper layers as θ_g increases. As a result, θ_g dependencies of characteristic x-ray emission depend on the depth of atoms that emit x rays. Figure 1 shows θ_g dependencies from various layers in a 6-ML Ga film on an Si substrate calculated by Monte Carlo simulation [13,14]. The details of the calculation are described in a previous paper [8]. Each θ_g dependence shows a maximum, and the position of the maximum shifts to higher θ_g as the depth increases. Thus, depth of an element can be analyzed from θ_g dependencies of x-ray emission.

Figure 2(a) shows a RHEED pattern of an Si(111)- α -($\sqrt{3} \times \sqrt{3}$)-Au surface. After 1 ML of Ga deposition on this surface ($\Theta_{\text{Ga}} = 1$), 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. 2(b) ($\theta_g = 2.5^\circ$). Figure 3(a) shows θ_g dependencies of GaK, AuM, and SiK characteristic x-ray emissions taken from this surface. Since the diameters of the incident electron beam and the sample were about 0.15 and 12 mm, respectively, the entire beam fell on the sample at θ_g above 0.7° . The rapid decreases in x-ray yields below $\theta_g = 0.7^\circ$ are due to the finite size of the sample. Above 0.7° , GaK intensity decreases quickly with increases in θ_g . On the other hand, AuM intensity increases, reaches a maximum at $\theta_g = 1.5^\circ$, and then decreases. These results indicate that Ga atoms exist in the uppermost layer and that Au atoms exist at the second

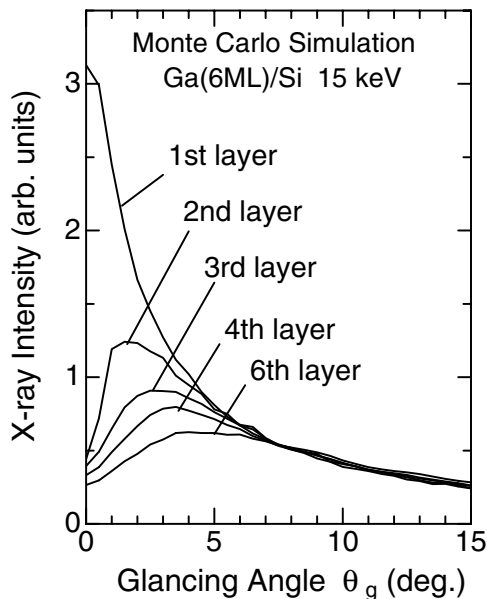


FIG. 1. θ_g dependencies of characteristic x-ray emission from various layers in a 6-ML Ga film on an Si surface calculated by Monte Carlo simulation. The position of maximum shifts to higher θ_g as the depth of the layer increases.

layer, conserving the $\sqrt{3} \times \sqrt{3}$ periodicity. SiK shows a broad maximum at 8.5° , indicating that Si atoms exist at deeper regions. The solid lines in Fig. 3(a) are θ_g dependencies of AuM and GaK calculated by Monte Carlo simulation, assuming that Ga atoms and Au atoms exist in the first and second layers, respectively. These lines agree well with the experimental results.

After further deposition of 1 ML of Ga ($\Theta_{\text{Ga}} = 2$), a RHEED pattern still showed spots of α - $\sqrt{3} \times \sqrt{3}$ structure at $\theta_g = 2.7^\circ$. However, a RHEED pattern taken at low θ_g of 0.5° showed transmitted spots characteristic of islands, as shown in Fig. 2(c). These results indicate that islands had formed but that the other parts of the surface were flat, conserving the α - $\sqrt{3} \times \sqrt{3}$ structure. A lattice constant of about 6 Å was obtained from these spots. This value is close to the lattice constant (6.06 Å) of AuGa₂ grown with its [111] direction parallel to the [111] direction of the substrate Si crystal. θ_g dependencies of x-ray emission taken from this surface are shown in Fig. 3(b). GaK decreases quickly with increases in θ_g , but AuM has a maximum at 2° . These results indicate that Ga atoms exist on Au atoms. However, analysis by Monte Carlo simulation suggests partial alloying between Au and Ga. The dashed line in Fig. 3(b) shows calculated θ_g dependence of AuM assuming that 2 ML of Ga exists on the Au layer. The shape of this line deviates downward from the experimental results below 3° . This disagreement was improved by assuming partial alloying; that is, about 30% of Au (2/9 ML) was exchanged with Ga in the nearest upper layer. The calculated θ_g dependencies of GaK and AuM with this assumption agree with the experimental results, as shown by solid curves in Fig. 3(b). This simulation indicates only the degree of alloying, and the assumed atomic structure in the simulation is not the actual structure. Considering the results of θ_g dependencies and RHEED observation [Fig. 2(c)], it is thought that Ga exists on Au but that partial alloying between Ga and

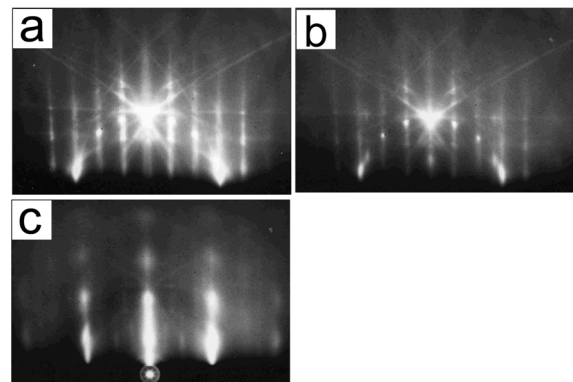


FIG. 2. RHEED patterns taken during deposition of Ga on an Si(111)- α -($\sqrt{3} \times \sqrt{3}$)-Au surface at room temperature. (a) Si(111)- α -($\sqrt{3} \times \sqrt{3}$)-Au. $\theta_g = 2.5^\circ$; (b) $\Theta_{\text{Ga}} = 1$ and $\theta_g = 2.5^\circ$; (c) $\Theta_{\text{Ga}} = 2$ and $\theta_g = 0.5^\circ$.

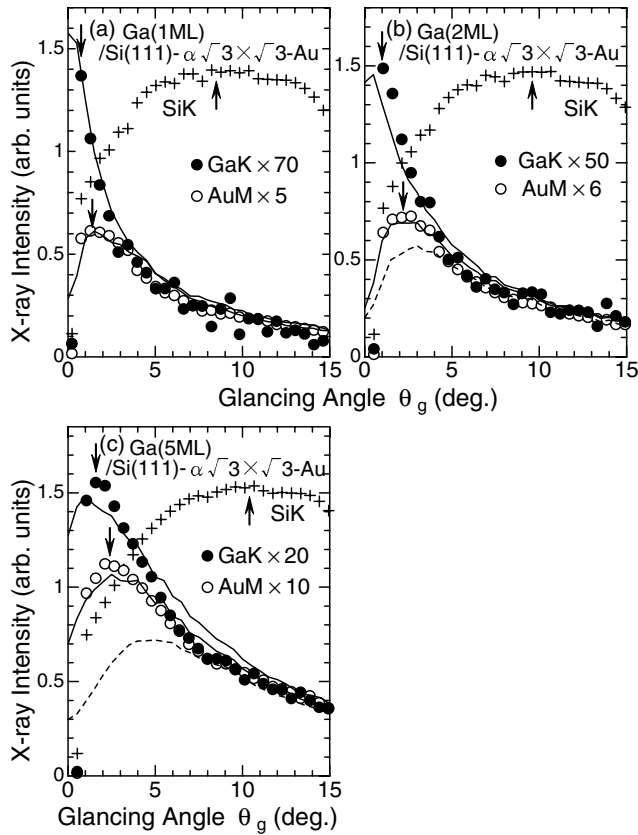


FIG. 3. θ_g dependencies of characteristic x rays GaK, AuM, and SiK measured during growth of Ga on an Si(111)- $\alpha\sqrt{3}\times\sqrt{3}$ -Au surface at room temperature. Peak positions of the θ_g dependencies are indicated by allows. (a), (b), and (c) are results at $\Theta_{\text{Ga}} = 1$, $\Theta_{\text{Ga}} = 2$, and $\Theta_{\text{Ga}} = 5$, respectively. Solid lines are θ_g dependencies of GaK and AuM calculated by the Monte Carlo method assuming the growth model (see the text). Dashed lines are calculated θ_g dependencies of AuM assuming that Ga grows on Au without intermixing between Ga and Au.

Au occurred, resulting in the formation of some AuGa₂ islands.

The alloying between Ga and Au became more significant with further increases in Ga coverage. A RHEED pattern taken at $\Theta_{\text{Ga}} = 5$ showed transmitted spots but no spots/streaks of the $\alpha\sqrt{3}\times\sqrt{3}$ structure, indicating that more AuGa₂ islands had formed and that the $\alpha\sqrt{3}\times\sqrt{3}$ structure had been completely destroyed. Weak rings of halo patterns, suggesting the existence of excess liquid Ga, were also seen. Figure 3(c) shows θ_g dependencies taken at $\Theta_{\text{Ga}} = 5$. The maxima of GaK and AuM are seen at 1.5° and 2°, respectively, and the shapes of these θ_g dependencies are similar. The dashed line in Fig. 3(c) shows calculated θ_g dependence of AuM assuming that 5 ML of Ga exist 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 intensity of GaK was enhanced more than that of AuM at lower θ_g , indicating that upper

parts in the film contain more Ga than do deeper layers. The solid lines in Fig. 3(c) show calculated θ_g dependencies of AuM and GaK assuming that Au and Ga are mixed but that the concentration of Ga in the first and second layers is 1.2 times higher than that in the third to sixth layers. These curves can explain the experimental results for both GaK and AuM. 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)- $\alpha\sqrt{3}\times\sqrt{3}$ -Au surface is proposed as shown in Fig. 4. After 1 ML of Ga deposition, a flat Ga film grows on the Au film with a $\sqrt{3}\times\sqrt{3}$ periodicity [Fig. 4(b)]. When Θ_{Ga} further increases, Au atoms dissociate from the $\alpha\sqrt{3}\times\sqrt{3}$ -Au structure, and alloying between Ga and Au occurs, resulting in the formation of AuGa₂ islands [Fig. 4(c)]. The $\alpha\sqrt{3}\times\sqrt{3}$ -Au structure has been completely destroyed at $\Theta_{\text{Ga}} = 5$. The excess Ga is thought to form droplets. In this growth, a critical Ga coverage exists around 1 ML, above which dissociation of Au and alloying between Ga and Au occur.

Alloying of a grown metal with a precovered metal was previously observed in the growth of Ga on an Si(111)- $2\sqrt{3}\times 2\sqrt{3}$ -Sn surface, which is formed by 1 ML of Sn deposition on an Si(111) surface [15]. In this growth, intermixing between Ga and Sn had already occurred at $\Theta_{\text{Ga}} = 1$, resulting in the formation of a flat film of Ga-Sn alloy. After further deposition of Ga, Ga grew into a liquid of Ga-Sn alloy. However, in the growth of Ga on an Si(111)- $\alpha\sqrt{3}\times\sqrt{3}$ -Au surface investigated in the present study, Ga initially grew into a flat overlayer on the Au layer, and alloying between Ga and Au occurred only at $\Theta_{\text{Ga}} > 1$. The existence of critical coverage above which different growth motions start have been suggested in some reports. In the growth of Au on an Si(111) surface, it was suggested that Au silicide layers formed above a critical coverage of about five Au monolayers [16,17]. It has been proposed that Si-Si bond breaking is induced by the screening effect due to metallic electrons in Au films that form above this critical coverage, resulting in intermixing between Au and Si, which is called a “screening model.” Also, in the growth of Ge on an Si(111) surface covered by Pb, substitution between Ge and Pb occurs, resulting in the formation of two-dimensional Ge islands covered by Pb, and it has been proposed that this substitution occurs only when local Ge coverages exceed a certain critical value [18,19]. In other words, only Ge atoms in a cluster form can dive below a Pb layer. As a result, the density of Pb-covered Ge islands increases rapidly above a Ge coverage of about 0.14 ML. The critical coverage of about 1 ML in the Ga/Au/Si system in the present study seems to be too small for formation of metallic electrons of Ga and is rather different from the critical coverages in Au/Si

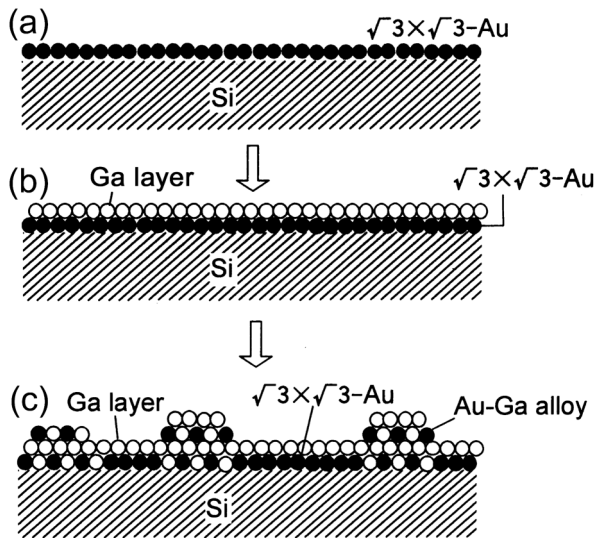


FIG. 4. A growth model of Ga on an Si(111)- α - $(\sqrt{3} \times \sqrt{3})$ -Au surface at room temperature. At the initial stage, Ga grows on the Au layer and the $\sqrt{3} \times \sqrt{3}$ periodicity is conserved. Above a critical Ga coverage of about 1 ML, Au dissociates from the $\sqrt{3} \times \sqrt{3}$ -Au structure, and alloying between Ga and Au occurs.

(5 ML) and Ge/Pb/Si (0.14 ML) systems. Thus, the origin of the critical coverage in the present Ga/Au/Si system seems different from those of Au/Si and Ge/Pb/Si systems.

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 Θ_{Ga} to high Θ_{Ga} . On the other hand, in the Ga/Au/Si system, the resultant alloy has a well-ordered structure of an AuGa₂ crystal, and eight Ga atoms are needed to form one unit cell of AuGa₂. Thus, some critical local Ga coverage may be required to supply a sufficient number of Ga atoms for alloying. Although $4/3$ ML of Ga can react with $2/3$ ML of Au in the α - $\sqrt{3} \times \sqrt{3}$ -Au structure, the $\sqrt{3} \times \sqrt{3}$ spots remained in RHEED pattern even at $\Theta_{\text{Ga}} = 3$ – 4 , indicating existence of excess Ga. Another possibility is that the surfaces of AuGa₂ islands are terminated by Ga atoms, which requires more than $4/3$ ML of Ga. Further experimental and theoretical works are required to determine the growth mechanism.

In summary, by RHEED observation and analyses of atomic depth distribution, the growth mode of Ga on an Si(111)- α - $(\sqrt{3} \times \sqrt{3})$ -Au surface at room temperature

was studied. It was found that a 1-ML Ga overlayer grew on the Au layer with a $\sqrt{3} \times \sqrt{3}$ -Au periodicity, and that dissociation of Au and formation of an Au-Ga alloy occurred above a critical Ga coverage of about 1 ML. Growth motions of atoms during epitaxy of the delta-doping type have not been elucidated. The present results provide a new example of such growth processes.

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