RHEED intensity oscillation during epitaxial growth of Ag on Si(111) surfaces at low temperature

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Epitaxial growth of Ag onto the Si(111) surface was studied using reflection high-energy electron diffraction. To understand the mechanism of epitaxy, its dependence on the substrate temperature and deposition rate was systematically investigated. The change in the intensity oscillations when the temperature is decreased from room temperature to 160 K was seen to be identical to intensity oscillation changes observed while increasing the deposition rate from 4.02 to 60 ML/min holding substrate temperature constant. The intensity oscillations are irregular up to 6 ML and become regular above 6 ML. The regular period after the growth of 6 ML is smaller than the thickness of the Ag(111) layer. A model for Ag growth on the Si(111)-7×7 surface at 160 K is proposed. The changes in periodicity are attributed to island and defect formation.

I. INTRODUCTION

Epitaxial growth of Ag on the Si(111)-7×7 surface has been extensively studied. Gotoh and Ino made a two-dimensional (2D) phase diagram for the Ag/Si(111) using reflection high-energy electron diffraction (RHEED). \(^1,^2\) When Ag was deposited onto the Si(111)-7×7 surface at room temperature (RT), elongated rodlike lines were observed, due to the texture structure of Ag epitaxial film with the preferential orientations of \((111)_{\text{Ag}} \parallel (111)_{\text{Si}}\) and \([011]_{\text{Ag}} \parallel [011]_{\text{Si}}\). Using scanning tunneling microscopy (STM), Tosch and Neddermeyer observed Ag clusters deposited at RT only on the faulted halves of the 7×7 unit cell in the dimer-adatom-stacking fault (DAS) model at low coverage, and epitaxial islands with different heights at higher coverage. \(^3\) STM \(dI/dV\) measurements revealed the Ag-Si interactions to be weak in the Ag clusters formed. Ultraviolet photoelectron spectroscopy (UPS) showed a reduction of measured local density of states at \(E_F\), indicating saturation of dangling bonds of the 7×7 structure by Ag atom adsorption. \(^3\)

Since the layer-by-layer growth could not be reached at RT, RHEED intensity oscillation would not be observed at this temperature. Jalochowski and Bauer observed RHEED intensity oscillations when Ag, Au, and Pb were deposited onto the 7×7 surface at low temperature (95 K). \(^4,^5\) They concluded that the growth of Ag is by layer-by-layer growth, since each peak of the RHEED intensity oscillations corresponded to a thickness of 1 ML. Recent, STM observations at 80–100 K showed 2D layerlike growth. \(^8\) The first layer was percolated by Ag atoms, which nucleated on both faulted and unfaulted halves of the 7×7 unit cell. After 3.6 ML of growth, 2D islands could be observed. The typical island size was about 30–40 Å. This growth mode might affect the surface conductivity. \(^9,^10\)

This paper reports an RHEED study of epitaxial growth of Ag on the Si(111) surface. To understand the mechanism of epitaxy at low temperature, we systematically studied its dependence on the substrate temperature and the deposition rate. The change in the intensity oscillations when the temperature is decreased from RT to 160 K was seen to be identical to intensity oscillation changes observed while increasing the deposition rate from 4.02 to 60 ML/min holding substrate temperature constant. Even at RT, the RHEED intensity oscillations can be observed when the deposition rate is large enough. At low temperature, the intensity oscillations are irregular up to 6 ML and become regular above 6 ML. The regular period after the growth of 6 ML is smaller than the thickness of the Ag(111) layer. A model for Ag growth on the Si(111)-7×7 surface at 160 K is proposed. The changes in periodicity are attributed to island and defect formation.

II. EXPERIMENTAL METHOD

A UHV chamber equipped with an RHEED system was used in this study. The residual gas pressure of the UHV chamber was less than \(5 \times 10^{-10}\) Torr except during Ag deposition, at which time the vacuum was \(\sim 7 \times 10^{-9}\) Torr. The electron beam energy of RHEED was 15 keV. The substrates were \(p\)-type Si(111) wafers with a resistivity of 50 \(\Omega\) cm and the size was 25×4×0.4 mm\(^2\). A clear 7×7 RHEED pattern of the surface was observed by heating the sample to 1200 °C several times. Ag was deposited onto the 7×7 structure using an alumina-coated basket. Deposition rates were monitored with a quartz-crystal oscillator. The deposition rate was changed from 0.01 to 60 ML/min. The uncertainty of the quartz-crystal oscillator was \(\sim 10\%\). A monolayer corresponds to approximately \(7.84 \times 10^{14}\) cm\(^{-2}\) Si atoms on the Si(111) surface.

A sample manipulator for low temperatures, which has a sample holder in a copper block and two vessels for liquid nitrogen, was used in this experiment. The sample temperature could reach about 80 K. After the Si wafer was heated to 1200 °C for cleaning, the sample was then cooled. Temperatures were measured by an Au-Fe thermocouple, which was clipped onto the block. There may have existed a temperature difference between the sample surface and the block. The RHEED intensity measurements were carried out by measuring the spot intensity of the RHEED pattern, focused to a photodiode detector with an optical system.
RHEED intensity changes during Ag growth on the Si \text{~} surface, as seen in Fig. 2 with increasing substrate temperature, only the first peak remains. With increasing thickness of Ag, the peak height decreases rapidly. With increasing to the first and the second peaks are 1 ML. With increasing temperatures were maintained at RT, 300 °C, 400 °C, and 500 °C, respectively. In Fig. 2, the periods correspond to dynamic effects.

From dynamic calculations, the calculated rocking curve along the (111) rod showed that the (222) diffraction spot intensity is not minimum. In this study, the specular beam intensity was measured during growth. For layer-by-layer growth on a stepped surface, the RHEED intensity oscillation can be observed at the out-of-phase (off-Bragg) condition, and is obviously within a small glancing angle (below 0.6°) of the incident beam. The glancing angle of the beam was set at near 0.4°, which corresponds to a reflection between (111) and (222) spots, and satisfies to the out-of-phase condition.

A. Temperature dependence (RT–500 °C) of RHEED intensity oscillations of Ag/Si(111)-7×7

Figures 1(a)–1(d) show RHEED patterns after the deposition of 6 ML. Figure 1(a) shows the long streaks and broad spots due to epitaxial layers of Ag. This is typical of the texture structure, which was analyzed by Gotoh and Ino. When the substrate temperature is increased above 300 °C, the \(v3\times v3\)-Ag structure is observed, as shown in Figs. 1(b), 1(c), and 1(d). Figures 2(a), 2(b), 2(e), and 2(d) show the RHEED intensity changes during Ag growth on the Si(111)-7×7 surface with a deposition rate of 4 ML/min. Sample temperatures were maintained at RT, 300 °C, 400 °C, and 500 °C, respectively. In Fig. 2(a) two intensity peaks are observed during the growth at RT. The periods corresponding to the first and the second peaks are 1 ML. With increasing thickness of Ag, the peak height decreases rapidly. With increasing substrate temperature, only the first peak remains as seen in Fig. 2(b). This surface shows a \(v3\times v3\)-Ag structure as shown in Fig. 1(b). At 400 °C and 500 °C, when Ag deposition is started, the RHEED intensities show a quick increase at first, and then do not show any change. The RHEED patterns correspond to that of the \(v3\times v3\)-Ag structure as seen in Figs. 1(b) and 1(d), and the spots become sharper. This implies that the deposited Ag atoms do not form 2D nuclei on the terrace after the \(v3\times v3\) formation. According to the scanning electron microscopy (SEM) observation by Endo and Ino, the \(v3\times v3\)-Ag domains form along step edges and become larger with increasing temperature, resulting in the sharp \(v3\times v3\)-Ag spots.

B. Temperature dependence (RT–160 K) of RHEED intensity oscillation

Figure 3(a) shows a 7×7 pattern at 160 K, and Figs. 3(b), 3(c), 3(d), and 3(e) show the RHEED patterns during the growth of Ag at 160 K, with the thicknesses of 1.0, 2.0, 3.0, and 20 ML, respectively. The growth rate was 4 ML/min. With increasing thickness of Ag, 7×7 spots become weaker, and the crystal reflections of Ag gradually appear and become stronger. These growth patterns are similar to that obtained at RT, but spots are broader, indicating that the growth domains are small. When the sample was rotated, the streaks remain observable in all azimuthal orientations, but their intensities change with the azimuthal angle. This indicates a texture structure, the same as observed at RT as described in Ref. 1. The elongated spots in Fig. 3(e) consist of double spots that are due to two domains with (111) orientation and a twin relation. When this sample was heated at 200 °C, the pattern changes as shown in Fig. 3(f). The \(v3\times v3\)-Ag structure and Ag crystal reflections can be seen.
This indicates that small 3D crystals of Ag grow on the \( v3\times v3\)-Ag surface and form a Stranski-Krastanov (SK) structure.

Figure 4 shows the intensity changes during the growth of Ag when the sample temperature was decreased to 260, 220, and 160 K, respectively. The periods in oscillations for each peak are summarized in Fig. 5. With decreasing temperature, many oscillation peaks are observed, and peak positions have a delay. In each case, the period corresponding to the first peak is 1 ML. At the first stage of the growth of 6 ML, irregular oscillation periods are observed. With decreasing temperature, the second peak is small, and the period changes from 0.55 ML (RT) to 1.15 ML (160 K). Then, the periods of the third and fourth peaks become large and reach the maximum value of 2.2 ML at 160 K. After the growth of 6 ML, the periods become regular, but still are smaller than the Ag[111] thickness of 1.76 ML. The measured period increases from 1 ML at 300 K to 1.45 ML at 160 K.

C. Deposition rate dependence of RHEED intensity oscillation at RT and 160 K

Figure 6 shows the RHEED intensity oscillations observed while depositing Ag onto Si[111]-7\( \times \)7 at RT. Deposition rates are 1.5, 4, 10.2, and 30 ML/min, respectively. With increasing rate, the RHEED intensity oscillations become prominent, with the number of peaks increasing from 2 (4 ML/min) to 10 (30 ML/min). In each case, the periods corresponding to the first peak are 1 ML. Even at RT the RHEED oscillations with more than 10 peaks can be observed when the deposition rate is 30 ML/min. This shows that, if the deposition rate is large enough, the growth of Ag is similar to that seen at low temperature.

Figure 7 shows the RHEED intensity oscillations during deposition at 160 K. Deposition rates are 4.02, 10.2, 30, and 60 ML/min, respectively. Figures 7(d) and 4(d) are the same data. The periods in oscillations for each peak are summarized in Fig. 8. The irregular oscillation periods are also observed. The changes in the intensity oscillations shown in Fig. 4 and Fig. 7 are identical. We conclude, thus, that the change in the intensity oscillations when the temperature is...
decreased is identical to intensity oscillation changes observed while increasing the deposition rate holding substrate temperature constant.

D. Effect of RHEED intensity oscillations by interruption deposition of Ag onto Si(111)-7×7 at 160 K

When the deposition is interrupted during growth, the deposited atoms move to a more stable position. Hence subsequent growth is affected, and this change can be probed by observation of RHEED intensity oscillations. Thus deposition interruption can help us to understand diffusion of atoms on the surface.

Figure 9 shows RHEED intensity changes when deposition was interrupted during growth. The glancing angle of the beam is 0.6°. The curve A is an intensity oscillation without interruption. We stopped the deposition by a shutter at the highest peak position P1, corresponding to P in the curve A, and then restarted the deposition at P2. The time interval between P1 and P2 was ~10 s, which corresponds to the growth of 0.8 ML. The measured oscillation is given by the curve B. Curve B was shifted to the left to coincide with the starting point of curve A. Similarly, curve C was obtained by an interruption at point Q. We observed that the peaks of B and C curves shifted to the right, and the periods became larger.

IV. DISCUSSION

A. Temperature and deposition rate dependence of RHEED intensity oscillation

As seen in Fig. 2, when Ag was deposited onto the Si(111)-7×7 surface at RT, the RHEED intensity shows only two peaks. This indicates that it is difficult to continue the formation of 2D nuclei. The corresponding RHEED pattern with long streaks, as shown in Fig. 1(a), indicates a texture structure, which means the growth of small thin crystals of Ag with a preferential orientation. This conclusion is consistent with other studies by RHEED, UHV-SEM, and STM...
Additionally, Ag growth on the Si(111) surface at low temperature depends upon the substrate surface structure. In this experiment we did not observe any additional structure at 160 K during the initial stage of growth, except for the reflections due to the Ag(111) layers. However when Ag was deposited onto the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag structure at 160 K, we observed new reconstructions $\sqrt{21}\times\sqrt{21}$ and $6\times6$ between 0.19 and 1.7 ML.\textsuperscript{17} The growth structure is different from RT at which only 3D reflections of Ag due to SK growth could be observed.

**B. Irregular periods of RHEED intensity oscillation**

RHEED intensity oscillation for Ag/Si(111) was first observed at 95 K by Jalochowski and Bauer.\textsuperscript{5} They observed regular oscillations corresponding to 1 ML of the thickness of Ag(111), and concluded that layer-by-layer growth is realized. Roos and Tringides also measured the RHEED intensity oscillations, and the results showed that the first peak corresponds to 1 ML and that the oscillations from the second peak seem to be irregular, as in our case.\textsuperscript{18,19} Additionally, after the growth of 3 ML, the intensities did not show the oscillations. This might be related to the slow deposition rates used.

As seen in Figs. 5 and 8, the first four peaks show the irregular oscillations. Additionally, these irregular oscillations were also observed for Pb, Au, and Cu at low temperature.\textsuperscript{5–7,16} This phenomenon was not observed in the cases of Si/Si(111) and GaAs/GaAs(111), where constant periods were observed.\textsuperscript{20–25} Kinematics calculations for homoepitaxial growth indicated accurately that oscillation peaks correspond to 1 ML.\textsuperscript{13}

In the cases of Au and Pb on Si(111) irregular oscillations were observed at initial stages of growth. These irregular oscillations were explained to be related to alloy formation during growth.\textsuperscript{5–7} This explanation by considering alloy formation does not sufficiently account for the Ag/Si(111). Because the Ag-Si interface is considered to be sharp,\textsuperscript{4,26,27} Ag obviously does not form a silicide or an alloy with Si, as Cu, Au, and the other transition metals do.\textsuperscript{28–33} In our case, the irregular oscillations can be measured up to 6 ML. These could not be considered to be a result of alloy formation.

Even taking into account weaker interaction between Si and Ag atoms, this interaction is confirmed to be within 2–3 ML from STM. Local STM/\textit{dI/dV} measurements showed the semiconductor characteristic for the first layer and the metallic characteristic for above 4 ML.\textsuperscript{3} The $7\times7$ structure is not destroyed by Ag atoms and remains in a good arrangement during the growth of the first monolayer. From photoelectron emission and Auger \textit{LVV} line-shape spectroscopy, McKinley, Williams, and Parke suggested that the Ag-Si interface is an atomically sharp interface at room temperature.\textsuperscript{26} Since at low coverage, the Si 4\textit{d} emission is extremely sharp and consistent with emission from isolated atoms. From our RHEED observations, Ag reflections after growth of 1 ML could be observed on the patterns with the lattice constant of Ag(111). On the contrary, in the case of Cu/Si(111), there are 10.4\%, 8.1\%, and 7.1\% measured mismatches at the thicknesses of 1.0, 2.0, and 10.0 ML, with the lattice constant of Cu.\textsuperscript{16} The Si-Cu interface shows the existence of a silicide within 12 ML with bonding characteristics of $p$-$d$ hybridization.\textsuperscript{29–33} The Si-Au interface shows stronger alloy-like phases in fewer layers.\textsuperscript{28} These results mean that the
Si-Ag interaction is not adequate to affect deeper than 5-6 ML. Thus we tend to conclude that the irregular oscillations of Ag/Si(111) are due to the growth mode itself. We suppose that the Si-Ag interface is nearly steep, and we propose a model for the growth mechanism at 160 K as shown in Fig. 10.

In Fig. 4(d), the first peak period corresponds to 1 ML of Ag growth. We conclude that the saturation coverage for first layer is about 1 ML as shown in Fig. 10(a). According to STM observations by Meyer et al., Ag atoms during the initial stage of growth nucleate to the faulted and unfauluted halves in the DAS model of the Si(111)-7×7 structure.8,34 The corner holes of the first layer formed are not occupied, and this first layer is percolated. This is different from what was seen at RT, where Ag nucleation was seen only in the faulted half of 7×7. Thus Meyer et al. concluded that the first layer is percolated, and that the minimum coverage is between 0.75 and 1.0 ML. This is in agreement with the period of 1 ML that we measured. In addition, UPS data obtained at RT showed a reduction of local density of states at $E_F$ (Fermi energy), indicating saturation of dangling bonds of the clean Si(111)-7×7 surface by the Ag atoms.4 At RT, an STM image showed that the 7×7 is not destroyed by Ag clusters formed on the faulted half.3 This is why we were able to observe the weak 7×7 structure in the RHEED pattern following the deposition of 1 ML of Ag.

The growth model proposed for the second peak is shown in Fig. 10(b). Here Ag atoms are located on the top of the first layer, which is percolated. Therefore the coverage is close to 1 ML of Ag. Additionally, Ag atoms may be more mobile than those in the first layer due to partial saturation of dangling bonds. Hence the mean free path of the Ag atoms of the second layer will be larger. This results in formation of islands at relatively high temperatures above 160 K. Without completing a full layer, the third layer will begin to form on the top, consequently, the period and the peak height of the second peak in the RHEED intensity oscillation will be small.

Figures 10(c) and 10(d) show the growth models for the third to the sixth peaks. A 2D layer of Ag(111) begins to form on the surface. Additionally, Ag islands grow partially between the growth of 2 and 6 ML on the third layer, as can be seen in area A, except for the 2D layer formed in area B. Therefore the oscillation period should be larger than the layer thickness of Ag(111) of 1.76 ML. In measurement, as shown in Fig. 9, the periods are seen to increase after the interruption. This indicates an increase of island formation after diffusion of atoms during interruption. This analysis is consistent with previous STM observation, where 2D layers were observed at 2.5 and 3.6 ML, however, Ag atoms at 3.6 ML tend to grow in the multilayer mode.6 As can be seen in Fig. 4(d), growth beyond 6 ML is characteristic with periodic oscillations. The growth of Ag layers occurs in a multilayer growth as shown in Fig. 10(e). The calculations for RHEED intensity oscillations show damping of intensities due to the multilayer growth.35–39 However, the observed period is 1.45 ML, smaller than the 1.76-ML thickness of Ag(111). This is attributed to defect formation during growth. The texture structure of Ag(111) at 160 K was seen in our RHEED pattern, indicating the formation of a number of small crystals of varying size and orientation on the surface. The Ag layers consist of a large number of domains with grain boundaries. The reflection spots were seen to be broader than those that were seen at RT, and indicate that the average domain size of Ag is smaller. The domain size $D$ is shown in Fig. 10(e). A thin strain region exists between the thick layers of the Ag and Si substrate on top of Si layer. This is due to the lattice mismatch between the Ag and Si. The RHEED pattern at this stage of growth consists of ill-defined reflections of Ag. At this stage, the dislocation lines may exist between two domains due to stress. In addition, growth may involve other types of the fault. Fault lines may form between two domains in some places in the layer, and faults may exist in the domains. Such gaps cannot be closed by a local readjustment, since filing the gaps causes another to appear. The local dislocations and faults exist along the domain boundaries and in the domains, resulting in a large number of plane defects such as holes and vacancies. In further growth of Ag, Ag atoms continue to grow on top of domains formed in the strain region. As a consequence, Ag layers consist of large numbers of small crystals of varying size and orientation, and plane defects continue to develop during growth. Therefore the thickness of the actual Ag layer will be smaller than the ideal thickness of a monolayer of Ag, 1.76 ML. This explanation is consistent with STM observations of Ag growth on Si(111)-7×7 at 80–100 K, in which partial dislocations at the step edge and stacking faults were observed at the thickness of 40 ML.8

In conclusion, the intensity oscillations during growth of Ag on Si(111)-7×7 surface at 160 K are irregular up to 6 ML, and become regular above 6 ML. The regular period above 6 ML is smaller than the thickness of the Ag(111) layer. We conclude that these changes in periodicity are attributed to island and defect formation.


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