Hydrogen-Mediated Epitaxy of Ag on Si(111) as Studied by Low-Energy Ion Scattering

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We have investigated the effect of the saturation of surface dangling bonds of Si(111) surfaces with atomic hydrogen upon Ag thin-film growth. By using time-of-flight-type low-energy ion-scattering–recoil analysis techniques, we find that the growth mode of Ag thin films is drastically changed by the hydrogen termination of Si(111)-7×7 surfaces and that the epitaxial growth of *A*-type Ag(111) films is promoted by the hydrogen atoms residing at the film/substrate interface.

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The growth of a metal thin film on a semiconductor substrate has attracted much attention from both fundamental scientific and practical viewpoints. A primary concern in obtaining good crystal growth is the growth mode or the crystallographic orientation of the film. There are three known modes of thin-film growth:[1] layer-by-layer growth [Frank–Van der Merwe (FM) mode], island growth [Volmer-Weber (VW) mode], and layer-plus-island growth [Stranski-Krastanov (SK) mode]. Which growth mode will be adopted in a given system will depend upon the surface free-energy terms and on the lattice mismatch. Modification of the substrate surface by the introduction of a foreign atomic layer that alters the surface free energy can change the growth mode of a film. Copel *et al.*[2] have proposed the use of a segregating As monolayer in the heteroepitaxial layer-by-layer growth of Si/Ge/Si(100). In the present paper, we will demonstrate growth-mode control of Ag thin films on Si(111)-7×7 surfaces by hydrogen termination of the Si substrate prior to the film growth. In comparison with the clean surface, the hydrogen-terminated surface reveals a different "substrate surface energy," and hence a different contact angle between the deposit and substrate, leading to the modification of the growth mode. Thus, hydrogen-terminated Si surfaces, which have been reported[3,4] to not only have a very low defect density but also be stable even in air, have been found here for the first time to also alter the growth process of metal thin films drastically.

The system of Ag thin films grown on a clean Si(111)-7×7 substrate is one of the most thoroughly studied systems so far.[5] It is widely accepted that at room temperature (RT) the growth proceeds basically in a layer-by-layer fashion (FM mode) and that at high temperature, beyond about 200 °C, the growth process turns to a SK mode with 3D island formation after completion of a 2D overlayer which displays a $\sqrt{3}\times\sqrt{3}$-$R30°$ periodicity. In this paper, on the basis of impact-collision ion-scattering spectroscopy (ICISS) with time-of-flight (TOF) detection, we report that (1) the above-described growth mode can be drastically changed by the atomic hydrogen termination of the Si substrate and (2) the epitaxial growth of single-domain Ag(111) planes is significantly promoted by the hydrogen termination. We call these phenomena hydrogen-mediated epitaxy (HME).

In usual ICISS,[6] ions scattered into the direction of the scattering angle range of 140°–170° are analyzed by electrostatic analyzers. Because of this specialization of the scattering angle close to 180°, ICISS allows one to analyze the atomic structure of solid surfaces straightforwardly.[6-11] However, ICISS performed by electrostatic energy analyzers involves, more or less, difficulties arising from the ion neutralization effect of noble-gas and alkali-metal ions. Since the difficulty can be excluded by the use of TOF-type energy analyzers which can detect both ions and neutrals scattered from the surface, several kinds of apparatus have recently been developed.[12-19]

Experiments were carried out in an ultrahigh-vacuum (UHV) system, equipped with TOF ICISS and low-energy electron-diffraction (LEED) apparatus. Since the TOF ICISS apparatus is described in detail elsewhere,[13-15] only an outline is given in this paper. A beam of He^+ produced by a differentially pumped ion source and mass separated by an electromagnetic mass analyzer can be chopped by two pairs of electrostatic deflection plates and a chopping aperture of 2 mm diameter. After passing through the chopping aperture, the pulsed ion beam hits the sample in the UHV chamber. The beam energy is in the range of 1.0–2.5 keV. The beam current and diameter are 10–30 nA and ~3 mm at the sample surface, respectively. Scattered ions and neutrals from the sample at a scattering angle $\theta = 180°$ (actually 179°–179.6°) can be detected by an annular-type microchannel plate (MCP) placed coaxially along the primary ion beam at a flight path of 60 cm from the sample. Energy analysis of scattered particles is made by measuring the time of flight between the sample and the detector by use of an eight-stop time-to-digital converter. Data are finally processed by a CAMAC system. In addition, TOF measurements can also be made for elastic recoil detection analysis (ERDA) using another MCP placed at a forward direction of a scattering angle of $\theta=14°$, enabling us to detect *in situ* hydrogen adsorbed on the specimen surface directly.

A P-doped, 17-23-Ω cm, $15\times35\times0.5$-mm^3 Si(111) wafer was preoxidized and cleaned *in situ* by direct heating at 1000 °C under a base presure on the order of $\sim10^{-10}$ Torr. After the cleaning, a sharp 7×7 LEED pattern was observed. Ag of 99.999% purity was evaporated from a tungsten conical basket heat at a deposition rate of roughly 0.3 ML/min, where 1 ML (monolayer) is defined to be 7.8×10^{14} cm^{-2}, the ideal Si density in the (111) plane. A 1800 °C tungsten filament, 10 cm from the Si surface, was used to dissociate molecular hydrogen. The exposures were made with the specimen facing the filament and by backfilling the chamber with H_2 at 1×10^{-6} Torr. The adsorption process of hydrogen has been measured by the TOF ERDA. After saturated adsorption at RT the chamber is evacuated to UHV and the growth process of Ag is studied by the TOF ICISS. The LEED pattern of the hydrogen-terminated surface is the so-called $\delta 7\times7$-H pattern as already reported. Upon Ag deposition at 300 °C the $\delta 7\times7$-H pattern gradually changes into a Si(111)-1×1 pattern accompanied with the epitaxially grown Ag(111)-1×1 pattern. The RT deposition showed a similar change, though the epitaxial Ag(111)-1×1 spots reveal the coexistence of azimuthally rotated small domains of Ag(111). It should be noted that the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag pattern cannot be formed[20] as long as adsorbed hydrogen exists on the specimen surface. These results of LEED observations have been reported before.[21] Our present ion-scattering results described below reveal the effect of the hydrogen termination and of the substrate temperature on both the growth process and the crystallographic orientation of Ag deposits.

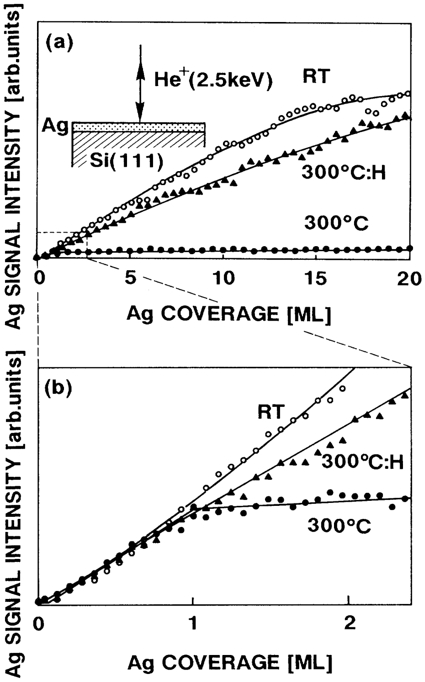


FIG. 1. Variations of TOF ICISS Ag signal intensities with the increase in Ag coverage (in ML) for three deposition conditions; data points labeled RT and 300 °C are for Ag deposition onto clean Si(111)-7×7 surfaces at the substrate temperatures of RT and 300 °C, respectively; those labeled 300 °C:H are for deposition onto hydrogen-terminated Si(111) surfaces at 300 °C. Results for the initial stage of film growth below ~2.5 ML are enlarged in (b). Note that there is a distinct difference between the data labeled 300 °C and 300 °C:H.

Figure 1 shows the variation of ICISS Ag peak intensities with the increase in Ag coverage for three different deposition conditions. The incidence direction of the 2.5-keV He$^+$-ion beam is normal to the specimen surface and the backscattered particles from Ag atoms are detected. As we can see, when Ag is deposited onto a clean Si(111) surface at RT, the Ag signal intensity increases linearly up to more than 15-ML coverage, indicative of the layer-by-layer growth mode of Ag films; the film being epitaxially grown Ag(111), as discussed later (Figs. 3 and 4). In contrast, when Ag is deposited onto a clean Si(111) at 300 °C, the Ag signal-intensity curve shows a sharp break point at around 1-ML coverage, which suggests the formation of 3D islands after the completion of a 2D layer (SK mode). These results on the film growth on clean Si surfaces agree well with many previous studies on this system.[5] The most important point of Fig. 1 is that when the Si surface is terminated with atomic hydrogen prior to Ag deposition, the Ag signal intensity at 300 °C increases almost linearly with no break point, suggesting that the growth mode still remains layer-by-layer-like even at the 300 °C substrate. The growth models derived in this study are schematically shown in Fig. 2. On the clean surface and at high temperature (300 °C), as shown in Fig. 2(a), deposited Ag initially forms the 2D layer of the $\sqrt{3}\times\sqrt{3}$-Ag structure, and surface diffusion of Ag atoms which impinge onto the $\sqrt{3}\times\sqrt{3}$ surface beyond 1-ML coverage probably occurs very rapidly, leading to coalescence into rather thick Ag islands. On the other hand, when the Si(111)-7×7 surface is terminated with atomic hydrogen of about 1.5-ML saturation coverage,[21] the Ag growth process becomes layer-by-layer-like and Ag islands formed are much thinner than those on the clean substrate case [see Fig. 2(c)]. The existence of hydrogen at the film/substrate interface, as depicted in Fig. 2, has been confirmed from the comparison of two ERDA experiments carried out by high-energy (MeV) and low-energy (keV) ion beams. High-energy ERDA experiments,[22,23] which can detect even buried hydrogen atoms, showed the hydrogen coverage of 0.5 and 0.3 ML after the deposition of 16-20-ML Ag at RT and 300 °C,

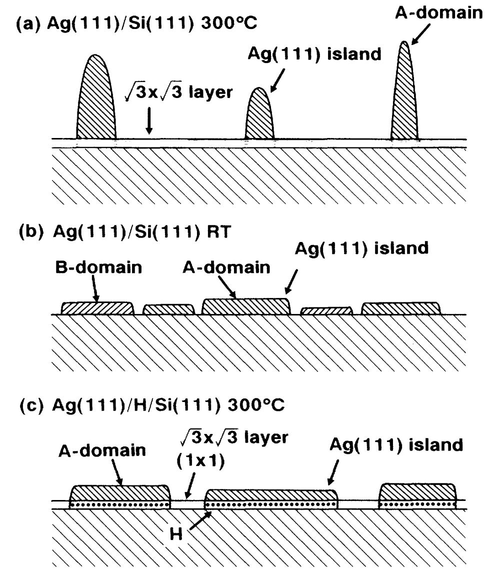


FIG. 2. Schematic illustration of the growth modes derived for three different deposition conditions of Ag on Si(111). (a),(b) Deposition onto clean Si(111)-7×7 surfaces. (c) Deposition onto a hydrogen-terminated Si(111) surface.

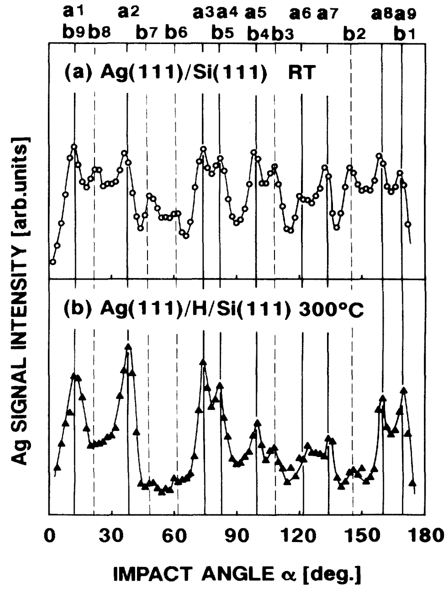
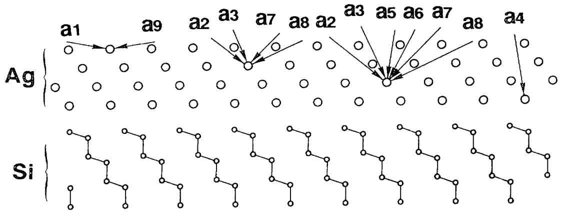


FIG. 3. TOF ICISS Ag signal intensities plotted against the impact angle α of incident ion beams (2.5 keV He^+). α is measured from the surface of the specimen. (a),(b) Deposition of Ag (40 ML) onto the clean surface at RT and onto the hydrogen-terminated surface at 300 °C, respectively. α values labeled a_1–a_9 and b_1–b_9 are those where intensity peaks are expected to appear for A-type and B-type domains of Ag(111) films, respectively (see Fig. 4 and text). Note that the experimental data given in (b) involve only the peaks labeled a_1–a_9.

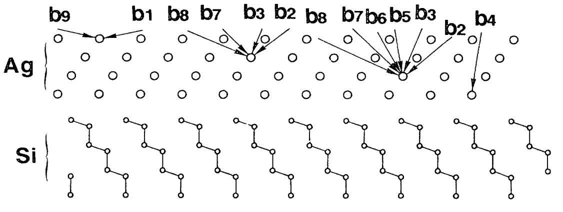
respectively.[21] On the other hand, low-energy ERDA experiments,[15] which can detect only hydrogen atoms on the topmost surface, showed a very small amount of hydrogen for both deposits. These two kinds of ERDA results reveal the presence of most hydrogen atoms at the interface of the Ag deposit and the Si substrate. LEED observations on Ag films grown on the hydrogen-terminated substrate at 300 °C reveal that the Ag islands are epitaxially grown Ag(111) planes and that a part of the substrate surface is not covered by the epitaxial Ag(111) islands, since LEED spots of both Ag(111) and Si(111) have been observed.[21]

Another important point schematically shown in Fig. 2 is preferred growth of so-called A-type Ag(111) planes on the hydrogen-terminated surface, derived from TOF ICISS angle scans described below. Figure 3 shows the variations of TOF ICISS Ag signal intensity as a function of impact angle α measured from the specimen surface, for two kinds of Ag(111) planes: (a) a Ag(111) film grown on a clean substrate at RT, and (b) a Ag(111) film grown on a hydrogen-terminated substrate at 300 °C. In Fig. 3, we can find many peaks of Ag signal intensity at various α's ranging from 0° to 180°. Since the ICISS peak intensity, in general, is strongly enhanced by the so-called focusing effect of ion beams,[6] we can explain all the observed peaks by the focusing effect at several specific incident directions of ion beams. If we divide the observed peaks of Fig. 3 into two groups, i.e., one group labeled a_1–a_9 and the other b_1–b_9, the group-a and group-b peaks can be explained to appear at corresponding α's as shown in Figs. 4(a) and 4(b), respectively. Figures 4(a) and 4(b) show side views of two kinds of Ag(111) films grown on Si(111) substrates, the former being a "A-domain" film, i.e., a film with parallel orientation Ag(111)[112]‖Si(111)[112], and the latter being a "B-domain" film, i.e., a film with a lattice orientation rotated 180° with respect to the substrate, Ag(111)[112]‖Si(111)[112]. It can be easily seen, for instance, that when α increases and approaches $\alpha = a_1$ ($\sim 10°$) the ICISS Ag signal intensity suddenly increases since all the topmost-layer Ag atoms step out from the shadow cone formed by the nearest-neighbor Ag atoms. In the same way, the appearance of other group-a peaks, as well as group-b peaks, can be interpreted. It is evident that the experimentally observed peaks of Fig. 3(a) involve both groups a and b and that those of Fig. 3(b) involve group a only. Thus, the experimental results given in Fig. 3 reveal that Ag(111) planes grown on the hydrogen-terminated substrate at 300 °C have a preferred orientation of type-A domain, while those grown on the clean surface at RT have mixed domains of type A and B, as depicted in Fig. 2.

The above-described results have clearly shown that the saturation of surface dangling bonds of the Si(111) surfaces with atomic hydrogen largely alters the growth process of Ag thin films. Although the reason why the epitaxial growth of Ag(111) films is promoted by the hy-



(a) Ag(111)[$11\bar{2}$]//Si(111)[$11\bar{2}$] : A-Domain



(b) Ag(111)[$\bar{1}\bar{1}2$]//Si(111)[$11\bar{2}$] : B-Domain

FIG. 4. Side view of the Ag(111) films epitaxially grown on Si(111) substrates: (a) *A* domain and (b) *B* domain. Incidence directions of ion beams, labeled a_1–a_9 and b_1–b_9, are those where the focusing effect is expected to appear for *A* and *B* domains, respectively.

drogen termination is not evident as yet, an enhanced surface migration of Ag atoms, together with an increased nucleation site density, over the hydrogen-terminated surface will promote the ordering of Ag deposits. The effect observed in this study seems to be similar to van der Waals epitaxy proposed by Koma, Sunouchi, and Miyajima,[24] where two materials having no dangling bonds on the surface can be a combination of a film/substrate system for excellent heteroepitaxy, regardless of the large lattice mismatch.

On the clean surface and at high temperatures (300 °C), surface dangling bonds are at first stabilized by the formation of a 2D adsorption layer of the $\sqrt{3}\times\sqrt{3}$- Ag structure, over which the nucleation site density is small and the surface migration of Ag seems to be too quick to form 2D-like thin islands of Ag(111), leading to rather thick Ag islands as shown in Fig. 2(a). It is to be noted here that the structure of the $\sqrt{3}\times\sqrt{3}$-Ag surface is readily changed into a Si(111)-1×1-Ag structure upon RT adsorption of atomic hydrogen, as already reported.[20] These structural changes induced by the hydrogen adsorption will cause HME through an increased nucleation site density accompanied by moderate surface migration of Ag atoms.

In summary, we have investigated the effect of the saturation of surface dangling bonds of the Si(111) surface with atomic hydrogen upon Ag thin-film growth. We found that the growth mode of Ag thin films is drastically changed by the hydrogen termination of Si(111)-7×7 surfaces and that the epitaxial growth of *A*-type Ag(111) is promoted by the hydrogen atoms residing at the film/substrate interface.

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