Growth mode and electrical conductance of Ag atomic layers on Si(001) surface

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Abstract

The difference in growth mode of Ag films at room temperature between on Si(001)-2 × 1 clean and Si(001)-2 × 3-Ag surfaces was studied by four-probe electrical resistance measurements, reflection-high-energy electron diffraction, low-energy electron diffraction, ultraviolet photoelectron spectroscopy and scanning tunneling microscopy. A peculiar change in resistance was observed during deposition of Ag on the 2 × 1 surface; the electrical resistance rose temporarily around 40 ML coverage, and then, it dropped steeply due to percolation among Ag islands. On the other hand, only a slow resistance drop was observed during Ag deposition on the 2 × 3-Ag surface. This difference in changes of electrical resistance was revealed to relate to the difference in Ag growth styles. Ag grew in island-growth mode with three-dimensional (3D) islands of Ag(1 1 1) and Ag(0 0 1) orientations up to around 40 ML coverage on the 2 × 1 surface, and Ag(1 1 1) islands dominated and percolated each other beyond this coverage. On the other hand, Ag grew only with Ag(0 0 1) 3D islands on the 2 × 3-Ag surface, among which the percolation occurred more slowly by further deposition. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ag films deposited on Si surfaces are well studied so far as an ideal metal/semiconductor system due to very small chemical interaction with an abrupt interface. This system is important also because of its technological and industrial interest in silicon device application. The Ag/Si(001) system is expected for application in fine silicon devices in the near future, because Si(001) is practically used as the substrates of microelectronics devices and Ag has the smallest electrical resistivity. In spite of these important properties of this system, there are comparably smaller number of studies on this system, while much more intensive studies have been devoted to Ag/Si(1 1 1) over the past two decades [1]. However, there has been a renewal of interest of Ag/Si(001) system recently

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by the observation of local- or long-range-order structures of a 2 × 3 phase and an “unwetting” phenomenon during the initial growth of Ag on Si(001) by scanning tunneling microscopy (STM) and low-energy-electron diffraction (LEED) studies [2–4].

Two different structure models have been introduced for the Si(001)-2 × 3-Ag surface by STM [4] and LEED studies [5], based on Ag coverage of 1/3 and 1/2 monolayer (ML), respectively. The surface band structure study suggests the coverage of 2/3 ML in order to explain its semiconducting character [6]. Thus Ag coverage of this surface is not yet clarified, though the coverage is estimated to be roughly around 1/2 ML in all these models.

Since atomically flat single-crystalline metal films are needed to explore the properties of metal films, many attempts have been made to prepare such films. One way to make such Ag films is the deposition on a cold substrate, followed by annealing up to room temperature (RT), resulting in an atomically uniform Ag layers [7]. Similar growth mode is also observed in Ag/Si(1 1 1) system [8], and is called “electric growth” mode [9] because electronic energy in the Ag film is considered to play a critical role in this growth mode. This mode is also observed for Ag films on the Si(001)-2 × 1 clean surface [10]. In all of these cases, the substrates should be cooled down to about 100 K during deposition.

In addition, the film of Ag(1 1 1) developed on Si(001) is not a perfect single-crystal film because of the lattice mismatch (2.2% error for “3√3-to-4” matching condition) [7]. On the other hand, Ag(001) film developed on Si(001) surface is expected to form a single-crystalline film due to much smaller lattice mismatch (0.2% for “3-to-4” matching condition).

In many cases, on the other hand, it is known that the metal films grow in quite different ways depending on the substrate surface structures. The Mn/Si(11 1) and Bi/Si(1 1 1) cases [11,12] are good examples. Especially in the case of Bi film on a Si(1 1 1)−√3 × √3-Bi surface, Bi single-crystalline epitaxial films were actually achieved, while such films were not obtained on a Si(1 1 1)−√3 × √3-Bi surface. The Ag films developed on a Si(1 1 1)−√3 × √3-Ag surface was very different in structure from those on Si(1 1 1)-7 × 7 clean surface [13,14]. Therefore, we expected from these facts that Ag single-crystalline films grown on a Si(001)-2 × 1 clean substrate will be different from on the Si(001)-2 × 3-Ag surface.

In this paper, we show the difference in Ag film growth modes between on the 2 × 1 clean and on the 2 × 3-Ag surfaces at RT, and discuss the relation between the growth modes and changes in electrical resistance during the growths.

2. Experimental

The experiments were done in three separate UHV chambers. The electrical resistance was measured in situ by a four-probe method [15], combined with reflection-high-energy electron diffraction (RHEED) in an UHV chamber. The ultraviolet photoemission spectroscopy (UPS) studies were done with LEED in an UHV chamber on the VUV beam line BL-7B (Research Center for spectroscopy, University of Tokyo) and Photon Factory, KEK, Japan. We used a commercial UHV-STM (UNISOKU) combined with RHEED at RT. All STM images were taken in the constant-current mode. All these measurements were performed at RT.

The substrates used were P doped n-type Si(001) wafers with 30–45 Ωcm resistivity at RT with 0.5 mm thick. The clean Si(001)-2 × 1 surface was prepared by heating up to 1500 K after outgassing at 900 K for 10 h. The surface was made smooth by annealing with direct current at 1300 K for 15 min. We etched the Si(001) substrate with so-called Ishizaka–Shiraki method [16] in the UPS studies before introducing it into the UHV chamber.

Silver was evaporated from outgassed alumina-coated tungsten baskets at a rate of about 1 ML/min. We estimated Ag coverage by assuming that the saturation coverage for the Si(001)-2 × 3-Ag superstructure was 1/2 ML. But, the coverage of this surface is still under debate as mentioned above. Therefore, there may be an error of about 20% at most in our Ag coverage estimation.
3. Results

3.1. Resistance changes

Fig. 1 shows typical resistance changes during depositions of Ag on the Si(001)-2 × 1 clean surface and on the Si(001)-2 × 3-Ag surface at RT. There are three interesting features in the case of the 2 × 1 clean substrate. First, the resistance decreases very slowly at Ag coverages up to around 35 ML. The second is an unexpected rise of resistance around 40 ML coverage. And the third is a very steep drop in resistance over 40 ML deposition. These changes can never be expected from a simple Stranski–Krastanov (S–K) growth mode of Ag films reported before [4,17,18], since the S–K growth mode is expected to show only a gradual and monotonous decrease of resistance with coverage due to the percolation among metal islands.

In contrast, in the case of the 2 × 3-Ag surface, the change in resistance is quite different; there is no rise in electrical resistance around 40 ML, and it drops more slowly beyond 40 ML.

3.2. Reflection-high-energy electron diffraction study

We observed changes in RHEED patterns during these Ag depositions on the two surfaces. The RHEED patterns in the case of the 2 × 1 substrate are shown in Fig. 2(a)–(c). In Fig. 3, the patterns of 50 ML-Ag films (a) on the 2 × 1 clean surface and (b) on the 2 × 3-Ag surface are compared.

Although in Fig. 2(b) diffractions spots and streaks from Ag crystals dominate the 2 × 1 superspots of the clean surface (Fig. 2(a)), the first

![Resistance changes of a Si(001) wafer](image1)

Fig. 1. Resistance changes of a Si(001) wafer during depositions of Ag on the 2 × 1 clean surface (solid line) and on the 2 × 3-Ag surface (broken line) at RT. The deposition rate was about 1 ML/min.

![RHEED patterns of Ag-adsorbed Si(001)-2 × 1 surfaces](image2)

Fig. 2. RHEED patterns of Ag-adsorbed Si(001)-2 × 1 surfaces at (a) 0 ML, (b) 5 ML, and (c) 50 ML coverages, respectively. They were taken with 15 keV electron beam in [1 1 0] incidence azimuth.
On the other hand, the RHEED pattern of Ag films deposited on the 2 × 3-Ag surface shown in Fig. 3(b) is different from Fig. 3(a). The streaks indicating Ag(111) flat-top islands are missing; only the transmission diffraction spots from fine Ag(001) crystals (indicated by white circles) with (111) and (331) facet lines are clearly observed (indicated by lines). This pattern suggests that the film on the 2 × 3-Ag substrate grows in island-growth mode only with 3D Ag(001) islands having (111) and (331) facets; there seems no Ag(111) islands grown.

To make it clearer how the Ag film grows on the 2 × 1 clean surface, we investigated the evolution of the RHEED spot intensity. Fig. 4 shows a change of intensity of a Ag(111) streak (indicated by a triangle in the inset RHEED pattern) relative to the intensity of a Ag(001) transmission spot (indicated by a circle in the inset) as a function of Ag coverage. From this graph we can say that the number of Ag(111) flat islands relative to Ag(001) 3D islands slowly increases with Ag coverage, and it jumps up around 40 ML coverage. This indicates that some of Ag(001) 3D islands are incorporated into Ag(111) flat islands, particularly around 40 ML coverage. This discontin-

Laue ring of the Si substrate can be seen as indicated by arrows. The RHEED patterns from Ag in Fig. 2(b) and (c) are consisted of a superposition of transmission diffraction spots from three-dimensional (3D) fine Ag crystals on the surface and reflection diffraction streaks from flat Ag(111) islands. The former spots are indicated by white circle in Fig. 3(a), which come form Ag islands epitaxially grown in (001) Ag/(001) Si relation, while the latter streaks are indicated by arrowhead in Fig. 3(a), showing (111) Ag/(001) Si epitaxial relation. There are also facet lines in the patterns originated from Ag(3 3 1) and Ag(1 1 1) facets (indicated by lines in Fig. 3(a)). We can say that these RHEED patterns are consistent with earlier works that the 3D islands nucleate with coverages over 1 ML and that the Ag atoms in two-dimensional layer are incorporated into the 3D islands (an unwetting phenomenon) [17].
uous change in structure seems to correspond to the resistance peak shown in Fig. 1. Such a structural change did not occur on the $2 \times 3$-Ag substrate.

3.3. Ultraviolet photoemission spectroscopy study

UPS was done for surfaces covered by various amounts of Ag on the $2 \times 1$ clean and also on the $2 \times 3$-Ag surfaces at RT. The spectra are shown in Fig. 5(a) and (b), respectively. They were taken with the incident photon energy of 20.5 eV, the incident angle $\theta_i$ was 45° from the surface normal with normal emission.

The states originated from the Ag wetting layer on the $2 \times 1$ substrate (shallow three peaks at 1, 2, and 3 eV below the Fermi level, indicated by arrowheads on the 0.5 ML spectrum in Fig. 5(a)) are also observed at 5 and 10 ML coverages in Fig. 5(a), which indicates that the surface is not yet wholly covered by Ag islands. A surface state inherent in Ag(111) surface at 0.1 eV below the Fermi level is observed only at 60 ML coverage (see the expanded spectrum as an inset). We also performed LEED observations on each sample before the UPS measurements. Only the 60 ML-coverage sample showed a double-domain Ag(111) fundamental LEED spots. Such spots were not observed at smaller coverages.

From these results, we can say that Ag grows on the $2 \times 1$ clean surface in a island-growth mode below around 40 ML coverage, while the islands having relatively wide and flat tops of Ag(111) face dominate at larger coverages.

On the $2 \times 3$-Ag surface (Fig. 5(b)), the surface state of Ag(111) was not seen even in the spectra of 60 ML coverage, indicating that Ag(111) islands do not grow. The $2 \times 3$-Ag surface states (shallow three peaks in the $2 \times 3$-Ag spectra in Fig. 5(b)) are observed very weakly on the spectrum at 5 ML coverage as indicated by arrows, meaning that the surface is not yet completely covered by the islands.

A large peak growing at 4–7 eV below the Fermi level is Ag 4d band, of which shape is quite different from each other in (a) and (b). This also means different growth styles of Ag films on the two substrates.

![Fig. 5. UPS spectra from (a) Si(001)-2 × 1 clean surface and (b) Si(001)-2 × 3-Ag surface, respectively, covered by Ag of coverages indicated on each spectrum.](image)

3.4. Scanning tunneling microscopy study

We acquired STM images of this system with various Ag coverages on the two substrates to confirm the Ag growth modes derived from RHEED and LEED-UPS studies described above. The images are shown in Figs. 6 and 7 for on the $2 \times 1$ clean and on the $2 \times 3$-Ag surfaces, respectively. Fig. 6(a)–(e) are the images of 1, 5, 10, 45
and 60 ML of Ag with the same scale, respectively. In the initial stage of Ag deposition (1 and 5 ML coverages), there appeared two kinds of islands. One is flat islands of nearly hexagonal shapes and the other is 3D islands of elongated shapes. The former ones are Ag(111) islands and the latter ones are Ag(001) 3D islands. Both of them grow larger with Ag deposition, but the substrate is not completely covered by the islands even at coverages more than 10 ML. The film morphology is very rough with the Ag(001) 3D islands having Ag(1 1 1) and Ag(3 3 1) facets at 45 ML coverage in (d). However, the image of 60 ML (e) shows a relatively smooth morphology, which is dominated by Ag(1 1 1) flat islands. The percolation paths appear to form around (d) and (e).
Fig. 7(a)–(c) are the images at 5, 10 and 20 ML Ag coverages, respectively, on the $2 \times 3$-Ag surface. The Ag(111) flat islands are not observed at all. The Ag(001) 3D islands with elongated shapes are slightly smaller in average size than on the $2 \times 1$ clean surface.

All these images are consistent with the results by RHEED and LEED-UPS described before. In this way Ag growth modes on the $2 \times 1$ clean surface and on the $2 \times 3$-Ag surface are clarified to be quite different.

4. Discussions

4.1. Growth modes

The models of Ag growth on the Si(001)-$2 \times 1$ clean surface and on the Si(001)-$2 \times 3$-Ag surface at RT, derived from the experimental results described above, are summarized in Fig. 8. At the initial stage of Ag deposition on the $2 \times 1$ clean surface, Ag grows in a S–K mode as reported in the previous STM studies [2,3]; Ag(111) islands grow after a wetting layer of 1 ML is completed. The Ag(111) islands have flat tops as seen by reflection diffraction streaks in RHEED patterns (Fig. 2). This is also confirmed in our STM study (Fig. 6). Our RHEED study revealed that Ag(001) 3D islands also grow in addition to the Ag(111) islands. Ag(111) flat islands dominate the Ag(001) islands very slowly with Ag coverage. This growth mode continues up to about 40 ML. But around 40 ML coverage, the morphology of the film changes discontinuously in a way that some of the Ag(001) 3D islands change into Ag(111) flat islands (Fig. 4). Then, the areal fraction of Ag(111) islands rapidly increases until the Ag(111) islands begin to percolate to make a smooth Ag(111) film (Fig. 6(e)).

On the $2 \times 3$-Ag substrate, on the other hand, the Ag film grows in a way illustrated in Fig. 8(b).
The Ag(001) islands have 3D shapes with (1 1 1) and (3 3 1) facets, with no Ag(111) islands coexisting. This growth mode with only Ag(001) 3D islands continues throughout the growth, and the islands slowly percolate each other beyond 40 ML, though the surface of the Ag film remains rough with the facets (Fig. 7(c)).

4.2. Lattice mismatch and surface energy

Ag/Si is a large lattice-mismatch system; the lattice constants of both of Ag(001) and Ag(111) faces are 2.889 Å, and that of Si(001) surface is 3.840 Å. But, these systems are nearly in “3-to-4” and in “3√3-to-4” matching conditions, respectively, which are illustrated in Fig. 9; the “3-to-4” matching condition means that a 4 × 4 cell of Ag(001) corresponds to a 3 × 3 cell of Si(001) surface. The “3√3-to-4” matching condition means that a rectangle 6 × 4 cell of Ag(111) corresponds to a 4 × 3 cell of Si(001) (see Fig. 9(b)). Then, in case of Ag(001) face, Ag lattice is only 0.2% larger than that of Si(001) substrate in both of [1 1 0]_Si and [1 1 0]_Si directions. In case of Ag(111) face, Ag lattice is 0.2% larger in [1 1 0]_Si direction, but 2.2% smaller in [1 1 0]_Si direction. Since these mismatches are relatively small in some directions, both of Ag(001) and Ag(111) islands can grow epitaxially on the Si(001)-2 × 1 surface in the initial stage. The interface energy, however, might be different between the two cases; Ag(111) islands may have a larger interface energy due to the larger lattice mismatch. Therefore from the point of view of interface energy, Ag(001) islands are preferable to grow.

Ag(111) surface is the most stable in all of the Ag surfaces because of the highest density of surface atoms. The Ag(111) flat islands have Ag(110) facets at their steep cliffs. Ag(110) surface has the second largest density of surface atoms and thus has the second smallest surface energy. The Ag(001) islands with (1 1 1) and (3 3 1) facets, on the other hand, have a larger surface energy. So, from the point of view of surface energy of Ag islands, Ag(111) islands will preferentially develop.
In case of the $2 \times 1$ clean surface, the S–K growth proceeds up to around 40 ML, which is consistent with the slow and monotonous decrease of electrical resistance at this range of Ag coverage: The wetting layer is not so conductive, and the 3D Ag islands percolate incompletely. On depositing Ag further around 40 ML, the Ag(001) 3D islands rapidly change into Ag(111) flat islands, which may temporarily break the partial percolation paths, resulting in the temporal increase in resistance. Soon after with more deposition, however, this also promotes the percolation among Ag(111) islands, resulting in the steep decrease of electrical resistance as observed in Fig. 1.

Another possible origin for the temporal rise of resistance around 40 ML coverage may be stress-induced resistance of the Si substrate. The lattice mismatch between Ag(111) islands and the Si(001) substrate is larger than that between the Ag(001) islands and Si(001) substrate as described above. Therefore, the stress caused at the Ag(111)/Si(001) interface is larger than that at the Ag(001)/Si(001) interface. This stress at the interface will increase the resistance of the Si substrate. The structure conversion from Ag(001) to Ag(111) islands would increase this effect of stress, which may cause the temporal rise of resistance of the Si substrate. But the percolation among Ag(111) islands occurred soon after causes the steep drop of resistance with further deposition.

In case of the $2 \times 3$-Ag substrate, on the other hand, the growth mode is much simpler; Ag(001) 3D islands just grow with Ag deposition. Around 40 ML coverage, the islands begin to percolate, but more slowly than on the $2 \times 1$ substrate, which corresponds to the slow decrease of resistance beyond 40 ML (Fig. 1).

4.3. Electrical resistance and growth modes

The changes of electrical resistance with Ag deposition on the Si(001)-$2 \times 1$ clean surface and on the Si(001)-$2 \times 3$-Ag surface are qualitatively explained by the growth models propose in Fig. 8.

Fig. 9. Lattice matching relations at (a) Ag(001)/Si(001) interface and (b) Ag(111)/Si(001) interface, respectively. Grey circles are Ag atoms, and white ones are Si atoms.

Thus, the transition from Ag(001) 3D islands to Ag(111) islands at around 40 ML coverage observed on the $2 \times 1$ clean substrate is caused by a transition in dominant factor from the interface energy at the Ag-islands/Si-substrate interface to the surface energy of the Ag islands. The preferable growth of Ag(001) islands on the $2 \times 3$-Ag substrate is due to the dominant effect of the interface energy throughout the whole process of growth.

5. Summary

By using four-probe electrical resistance measurements, RHEED, LEED, UPS and STM, the growth modes of Ag films from sub-monolayers to high coverages over 50 ML were studied on the Si(001)-$2 \times 1$ clean surface and on the Si(001)-$2 \times 3$-Ag surface at RT. The films grew in island structures.
growth mode up to about 40 ML on both surfaces: Ag(111) islands and Ag(001) 3D islands coexisted on the 2 × 1 clean surface, while only Ag(001) 3D islands grew on the 2 × 3-Ag surface. Some of Ag(001) islands transformed into Ag(111) ones on the former surface around 40 ML coverage, resulting in a relatively smooth mosaic Ag(111) film. In contrast, the Ag(001) islands on the 2 × 3-Ag surface did not “wet” in this way; the surface morphology of the films remained rough, having Ag(111) and Ag(3 3 1) facets. The observed peculiar changes in electrical resistance were qualitatively explained in terms of such a difference in growth style of the Ag films.

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