Abstract

Growth behavior of thin Ag films on Si substrates at room temperature has been investigated by scanning tunneling microscopy and reflection high energy electron diffraction. In the layer-plus-island growth Ag islands show strongly preferred atomic scale heights and flat top. At low coverage (1 ML), islands containing two atomic layers of Ag are overwhelmingly formed. At higher coverages island height distribution shows strong peaks at relative heights corresponding to an even number (2, 4, 6, ...) of Ag atomic layers. Beyond some coverage the height preference vanishes due to the appearance of screw dislocations and spiral growth.

Keywords: Overlayers on surfaces; Scanning tunneling microscopy; Preferential heights in island growth; Ag growth on Si

1. Introduction

The growth of Ag on Si has been widely studied as a model nonreactive metal–semiconductor system. Growth morphology has been found to depend on the deposition rate and growth temperature. For Ag deposition on Si(111)-(7×7) at low temperature (LT), reflection high energy electron diffraction (RHEED) oscillations were observed up to many monolayers (MLs) indicating a quasi-layer-by-layer growth [1,2]. Scanning tunneling microscopy (STM) studies on such samples also indicated quasi-layer-by-layer growth up to 3.6 ML [3]. This was attributed to a lower average island size and higher island density compared to room temperature (RT) growth. At RT deposition it is generally accepted that the growth follows the Stranski–Krastanov (SK) or layer-plus-island growth mode [4–7]. However, for RT deposition quasi-layer-by-layer growth has also been observed but only for high deposition rates (≈30 ML/min) [1]. Ag deposition at LT, followed by RT annealing, leads to yet another growth mode in which 3D plateau like Ag islands with a strongly preferred height are observed on a wetting layer [8]. The islands increase their number density and lateral extension with coverage with no change in height, eventually forming a percolated network of the same preferred height. This behavior was observed where 1 ML to a maximum of 2.2 ML deposition was studied [8]. This growth mode is different from the conventional SK growth mode. The role of electronic driving force has been suggested to be responsible for this mode of growth. Zhang and coworkers proposed the electronic growth mechanism, in which a uniform layer can be grown only over a thickness window; for film thicknesses below or above this window the metal film would be nonuniform [9,10]. According to their work, very thin films are destabilized by charge transfer at the interface, films of intermediate thickness are stabilized by...
quantum confinement and thick films are destabilized by stress. Huang et al. studied Ag growth on Si(111)-(7×7) at 50 K followed by annealing at 300 K [11]. By STM measurements they observed that flat pin-hole free films can be grown where the amount of material deposited exceeds 6 ML but multilayer pits are observed for thinner films. Growth at 300 K was found to produce three dimensional structures. These authors did not explore much higher film thicknesses to find out if there exists a thickness window above which the film again becomes nonuniform. To explore this aspect films of higher thicknesses are to be studied. The authors of Ref. [11] studied only a maximum thickness of 6.4 ML. Moreover, whether plateau like islands with a strongly preferred height can be formed with RT growth, as observed by Gavioli et al. [8] for LT deposition and RT annealing, has not been explored. In their study the thinnest Ag film on Si(111)-(7×7) grown at 300 K was 5 ML. Thinner films are to be studied to reveal any plateau like islands with a height preference.

For Ag film growth at RT and at low coverages (0.38–1.75 ML) a preference for the growth of islands with two atomic layers of Ag was observed, along with a significant fraction of islands with single-atomic-layer height for the lowest coverage [12]. These features have also been reported by Su et al. who studied growth of Ag films deposited at RT in the coverage range of 0.6–1.4 ML [13]. Growth features at RT deposition for higher coverages have not been reported by these authors [12,13].

Here we report on our RHEED and STM studies of growth of Ag films on Si(111)-(7×7) surfaces for RT growth over a wide range of film thicknesses. Encouraged by the fact that for other metal/Si systems LT [14] as well as RT [15] deposition shows growth of islands with preferred heights as a consequence of quantum size effect (QSE), we explore whether a height preference exists for the growth of Ag on Si over a range of thicknesses for RT growth. Indeed we observe growth of plateau like Ag islands with an N-layer (N even) height preference. We directly show that the Ag islands are (111) oriented. Our work also shows that the island height preference extends beyond two-atomic-layer height for thicker films in a quantized manner [16]. These aspects along with the detailed morphology are presented here.

2. Experimental details

Growth of Ag and RHEED and STM measurements were performed in a custom made molecular beam epitaxy (MBE) chamber coupled with an ultrahigh vacuum (UHV) variable temperature scanning tunneling microscope (VTSTM, Omicron). This system has been described elsewhere [17]. Base pressure in the growth chamber was $1 \times 10^{-10}$ mbar. Si(111) substrates were cut form n-type silicon wafers with resistivity in the range 10–20 $\Omega$ cm. After introducing into the MBE chamber, substrates were degassed at 600 $^\circ$C for about 12 h. The sample was then flashed briefly at ~1150 $^\circ$C to remove the native oxide and cooled slowly to RT. The characteristic structure of an atomically clean Si(111) surface, the (7×7) reconstruction, was observed by RHEED and STM. Ag was evaporated from a Knudsen cell (PBN crucible) and deposited onto the Si(111)-(7×7) surfaces, kept at RT, at the rate of 2 ML/min. (Some authors have defined a monolayer of Ag to be equivalent to the nominal surface atomic density of Ag[111], 1.5×10^{15} atoms/cm², as in Ref. [8]. Others have defined a monolayer to be the equivalent of the atomic density on an ideal Si(111) surface, which is 0.78×10^{15} atoms/cm². Here we use the former definition.) During deposition the chamber pressure rose to 8.5×10^{-10} mbar. RHEED measurements were made following each deposition and in some cases during deposition. Following deposition the sample was then transferred into the VTSTM chamber for microscopy measurements at RT. Film thickness was measured during growth by a quartz microbalance as well as post-growth Rutherford backscattering spectrometry (RBS) experiments.

3. Results and discussion

3.1. Growth and morphology

For a thin (1 ML) Ag layer grown on a Si(111)-(7×7) surface at RT, a STM image is shown in Fig. 1(a). A height scan along the line marked in Fig. 1(a) is shown below the image. Growth of flat-top islands with a preferential height is evident from the height scan. Indeed all the islands seen in Fig. 1(a) have the same height. Height distribution of Ag islands obtained from the micrograph in Fig. 1(a) is shown in Fig. 1(b). The dark background area (marked ‘A’) in Fig. 1(a), corresponding to peak A in Fig. 1(b), is the first Ag wetting layer on Si(111). The bright features (marked ‘B’) in Fig. 1(a), corresponding to peak B in Fig. 1(b), are Ag islands with flat top and a height of 5.4 Å from the Ag wetting layer. Fig. 2 shows the RHEED patterns from a clean Si(1 1 1) surface and following 1 ML Ag deposition. The RHEED pattern in Fig. 2(b) indicates that the Ag islands have grown in the (1 1 1) orientation. Assuming that the vertical spacing between atomic layers in the Ag islands is close to the corresponding value in bulk Ag along the [1 1 1] direction, the observed island height would contain two atomic layers of Ag. The wetting layer contains about 0.5 ML Ag [8], the remaining deposited Ag grows as islands on the wetting layer. So the double-layer height preference of the Ag islands is obvious. This height preference of Ag islands for RT growth of Ag on Si(111)-(7×7) surfaces is quite robust. Among several STM images, in one image similar to Fig. 1(a), among islands of double-layer height only one island of a height corresponding to three atomic layers of Ag was found. In these images we observed no Ag island of one atomic layer height. A significant fraction of islands of one atomic-layer height was observed in earlier studies for low coverages and much lower rate of deposition (~0.1 ML/min) [12,13] compared to our
case (2 ML/min). The root-mean-square roughness on any
given island is \( \sqrt{\frac{2}{C^2}} \) while that obtained from the whole
image (Fig. 1 (a)) is 2.2 Å. The double-layer height (5.4 Å)
preference of Ag islands for the Ag/Si(111)-(7·7) system
was earlier observed only for LT (150 K) deposition fol-
lowed by RT (300 K) annealing for deposition between 1
and 2.2 ML Ag [8]. This novel growth mode was qualita-
tively explained in terms of the electronic growth
mechanism [9,10], wherein the quantized electrons in a layer
can influence the morphology. As we observe here, for the Ag/Si(111)
system LT growth followed by RT annealing is not a necessary condition for the formation of islands of preferred heights. They are also formed in RT deposi-
tion. Other experiments at RT deposition also reported
preferential growth of double-layer islands, although with a
sizable fraction of one- and three-atomic layer islands

![Fig. 1. (a) STM image (700 x 700 Å²) of a 1 ML Ag film deposited on a Si(111)-(7·7) surface at RT. Sample bias voltage \( V_s = 2.1 \) V, tunneling
current \( I = 0.2 \) nA. Height profile along the line is shown (scales are in Å).
(b) Island height distribution obtained from the image in (a), showing the
strongly preferred height (peak B) corresponding to two atomic layers of
Ag(111). Peak A represents the Ag wetting layer.](image1)

[12]. Height preferences with larger heights have been ob-
served in other metal/silicon systems [14,15]. We have
investigated the growth of Ag layers of various thicknesses
(1–60 ML). For 2 ML Ag films preference for the growth
of islands of \( N \)-layer (\( N \geq 2 \)) height is observed. A height
distribution plot obtained from a STM image of a 2 ML

![Fig. 2. RHEED patterns: (a) from a clean Si(111)-(7·7) surface,
(b) following deposition of 1 ML Ag on a Si(111)-(7·7) surface. In (b)
Ag(111) spots are observed.](image2)

![Fig. 3. Height distribution obtained from of a STM image of a 2 ML Ag
film. Peak A corresponds to the wetting layer and B, C, D and E
 correspond to islands of monolayer, bilayer, trilayer and quadrilayer
heights, respectively. Islands of double-layer and four-layer heights are
dominant.](image3)
film is shown in Fig. 3. There is a strong tendency of height preference in units of bilayer height ($N = 2$ (A–C), $4$ (A–E)). From Fig. 3 we also notice the existence of monolayer (B) and trilayer (D) heights; however, their intensities are smaller. For the growth of 4 ML onwards, the Ag layer forms a percolating structure. The height distribution from a 5 ML Ag film is shown in Fig. 4. Growth of islands of $N$-layer ($N$ even: 2, 4, 6) height is prominent. The peaks A, B, C, D in Fig. 4 correspond to the wetting layer, $N = 2$, $N = 4$, $N = 6$ islands. These heights are seen in line scans through the STM image (not shown). STM images from 20 ML and 40 ML Ag films are shown in Fig. 5. Small hexagonal islands appear to grow on the outer layers beginning around 20 ML thick films. These hexagonal islands become more prominent for 40 ML and 60 ML (shown later) films. Height distribution from a small area (marked in Fig. 5(b)) in the 40 ML film is shown in Fig. 6. Even for this thickness the tendency of height preference for $\Delta N = 2$ is observed. However, for this relatively thicker film, a height distribution over large areas do not show a clear even-$N$ height difference. As we have mentioned earlier, there are hexagonal islands for 40 ML and 60 ML films. These islands show monolayer steps as shown in Fig. 5(b). An island marked ‘A’ in Fig. 5(b) (also shown in the inset in the light-shaded mode) shows the monolayer height features as seen in the height scan. Once the monolayer height is present, the height distribution will show both odd-$N$ and even-$N$ peaks. Moreover, screw dislocations and spiral growth appear in thicker films. One such example is shown in Fig. 7(a). Presence of such dislocations and the associated growth spirals introduces a continuous height distribution as suggested by the height variation shown in the box in Fig. 7(b). Thus a height distribution collected from a large image for film thicknesses $>20$ ML is considerably smeared.

Apparently the $N$-layer height preference with an even value of $N$ is an effect of quantum confinement of electrons in the Ag islands. To our knowledge in the existing literature neither theoretical nor experimental results (except for $N = 2$ in LT growth followed by RT annealing [8] and in RT growth for low coverages [12,13]) on the height preference in Ag(111) films on Si(111) substrates are available. Recently for Pb islands grown on Si(111) substrates, Okamoto et al. observed a preference for islands with height differences ($\Delta N$) equivalent to an even number of Pb atomic layers [15]. Surface energy has been found to be lower for a height containing an even number of atomic layers, compared to the neighboring heights containing an odd number of layers. For Ag films on Fe(100) surfaces, in general an $N$-layer film, though stable at low temperature, was found to bifurcate into a film with $N \pm 1$, i.e. $\Delta N = 2$. 

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Fig. 4. Height distribution obtained from a STM image ($350 \times 850 \text{ Å}^2$) of a 5 ML Ag film. $N$-layer heights of islands (B: $N = 2$, C: $N = 4$, D: $N = 6$) for even values of $N$ are strongly preferred.

Fig. 5. STM images of (a) 20 ML (1000 $\times$ 1000 Å$^2$) and (b) 40 ML (2000 $\times$ 2000 Å$^2$) Ag films. Height profiles along the marked lines are shown (scales are in Å). Small hexagonal islands on the top layer begins to grow for $\geq 20$ ML films. These islands are more abundant on 40 ML films. Such an island ‘A’ is shown in the inset of (b); the height profile on this island is also marked ‘A’. Monolayer steps are seen on this multi-tier island. When such features are included, odd $\Delta N$ peaks are also included in the relative height distribution.

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Fig. 6. STM image of a 40 ML Ag film. Height distribution from a small area (marked in Fig. 5(b)) in the 40 ML film is shown in Fig. 6. Even for this thickness the tendency of height preference for $\Delta N = 2$ is observed. However, for this relatively thicker film, a height distribution over large areas do not show a clear even-$N$ height difference. As we have mentioned earlier, there are hexagonal islands for 40 ML and 60 ML films. These islands show monolayer steps as shown in Fig. 5(b). An island marked ‘A’ in Fig. 5(b) (also shown in the inset in the light-shaded mode) shows the monolayer height features as seen in the height scan. Once the monolayer height is present, the height distribution will show both odd-$N$ and even-$N$ peaks. Moreover, screw dislocations and spiral growth appear in thicker films. One such example is shown in Fig. 7(a). Presence of such dislocations and the associated growth spirals introduces a continuous height distribution as suggested by the height variation shown in the box in Fig. 7(b). Thus a height distribution collected from a large image for film thicknesses $>20$ ML is considerably smeared.
Some theoretical attempts have been made to understand the $N$-dependent stability of metal films in terms of the energies of the quantum well (QW) states. The QW states are usually analyzed using a picture of standing waves within a potential well, in which energy-dependent phase shift upon reflection at the interface is included. For s–p metals the QW energy levels are often described by the phase accumulation model [19,20]. In order to apply this model to the Ag(111)/Si(111) case, one would need the Ag band structure (energy dispersion along the [111] direction) and the phase shifts at Ag/vacuum and Ag/Si interfaces. Although no theoretical results are available for the Ag/Si(111) system, it may be possible that the quantum size effect is important in leading to the observed height preference of the Ag islands.

For theoretical calculations, unlike many other cases (for example Pb), Ag(111) would pose an additional question whether the (111) neck in the Fermi surface, i.e. the deviation from the spherical Fermi surface, has an effect on the film stability. The theory also needs to consider the change of the Ag band structure due to strain induced by the Si(111) substrate due to epitaxy.

It is interesting to note that the bilayer height on the wetting layer for the thinnest Ag film (1 ML) is about 5.4 Å (Fig. 1). (The same value of the double-layer height was observed by Gavioli et al. [8] for film thicknesses between 1 and 2.2 ML. These authors did not study thicker films.) However, for the thicker films (see Figs. 3, 4 and 6) we observe some variation in the bilayer height separation. (It should be noted that the measured value depends somewhat on the magnitude of the sample bias voltage and its sign. However, the trend remains the same.) While for Ag islands on Si no report is available on thickness relaxation depending on the total number of atomic layers in an island, for Pb islands on Si(111) surfaces an oscillatory thickness relaxation was observed depending on the number of atomic Pb layers in the islands. This oscillatory thickness relaxation has been shown to be correlated with quantized electronic states in the Pb islands [14]. The thickness relaxation has been shown to be correlated with quantized electronic states in the Pb islands [14]. The thickness relaxation has been characterized in terms of the deviation from ideal thickness, defined as $\Delta t = t_N - N\delta_0$, where $N$ is the number of atomic layers on the wetting layer, $\delta_0$ is the ideal interlayer spacing and $t_N$ is the thickness of the island. For small $N$ the deviations were found to be large (for example, $\Delta t = -0.5$ Å, 0.2 Å and −0.4 Å for $N = 5$, $N = 6$ and $N = 7$ respectively).

Dislocations are a common defect in Ag layers due to the small stacking fault energy. They appear in thicker films. On the top of a 60 ML Ag film the presence of a screw dislocation and spiral growth around it are shown in Fig. 7(a). Height scans along three lines around the dislocation in the STM image of Fig. 7(a) are shown in Fig. 7(b). While away from the dislocation, step heights correspond to $\Delta N = 1$, there is a continuous variation of heights near the dislocation as indicated by the height profiles marked in the box in Fig. 7(b). Due to these features the relative height distribution from this sample shows hardly any height preference.

The theoretical prediction of the electronic growth mode [9,10] is that the film should be uniform over a thickness around 400 K [18]. Some theoretical attempts have been made to understand the $N$-dependent stability of metal films in terms of the energies of the quantum well (QW)
window. Within our limited search over selected thicknesses (1, 2, 4, 5, 10, 30, 40, and 60 ML) we have not observed uniform film growth. An extended search would be necessary to explore if there exists a thickness window over which a film of uniform thickness can grow at RT or any other growth temperature.

4. Summary and conclusions

We have studied growth of Ag on Si(111)-(7×7) surfaces at room temperature. Initial deposition of 1 ML Ag produces islands with a strongly preferred height of two atomic layers of Ag in the (111) orientation on the wetting layer. Thicker films show a tendency of growth of N-layer islands, where N is even (two, four, six, ...). Considering this growth feature, Ag growth on Si(111)-(7×7) at RT cannot be simply classified within the three commonly known growth modes. The electronic confinement apparently plays a role in determining the film morphology. As-deposited thicker films (>20 ML) show the formation of hexagonal islands at the top. Some of these islands appear to show screw dislocations and spiral growth. Presence of such islands destroy the height preference.

Within our limited search we have not observed, for RT growth, any thickness window for the uniform layer growth—a prediction from the electronic growth mechanism. Obviously an extended search over film thickness and growth temperature would be necessary to explore this aspect.

In order to understand the even-layer height preference of Ag islands on Si(111) surfaces, it is necessary to have theoretical investigations on this aspect. We hope that the interesting observations presented here will initiate a theoretical investigation for a proper understanding of these phenomena. Experimentally we have tried to understand height preference by making scanning tunneling spectroscopy measurements on islands of selected heights. In the local density of states, if we define a Fermi level ($E_F$) halfway between the highest occupied subband (HOS) and the lowest unoccupied subband (LUS), we find that this value of $E_F$ for the islands with even number of Ag atomic layers falls below the value of $E_F$ for bulk Ag. For the islands with an odd number of Ag atomic layers $E_F$ falls above the bulk $E_F$. This electronic energy lowering for the islands with an even number of Ag atomic layers is apparently responsible for their stability and their preferential growth [21]. Details of this aspect will be presented elsewhere.

References