Growth of ultrathin nanostructured Ag films on Si(111) 7 × 7: a SPA-LEED study

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Abstract

Ultrathin Ag films grown on Si(111) 7 × 7 at different temperatures have been studied by spot profile analysis of low energy electron diffraction (SPA-LEED). For a deposition temperature of 100 K the films consist of touching (111) oriented grains and are complete at a coverage of about 1 Ag monolayer. For deposition at room temperature, in contrast, the grains form separated islands. The grains show a rotational disorder of 6° and are atomically flat, as the rms height variations are only 10% of the atomic Ag interlayer spacing. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Growth; Low energy electron diffraction (LEED); Silicon; Silver; Surface structure, morphology, roughness, and topography

1. Introduction

Ultrathin films of silver grown on Si(111) 7 × 7 constitute an especially interesting system because Si(111) surfaces can be flat over distances of several micrometers, no silicide formation takes place, and the silicon substrate behaves at low temperature as an insulator. Ag films on Si(111) 7 × 7 can be grown epitaxially with unexpected quality, providing a very good model system to study electrical transport phenomena in two dimensions, which are of great interest in particular for applications in miniaturized integrated circuits. At a crystal temperature of \( T = 100 \) K scanning tunneling microscopy (STM) studies have shown that the film grows layer by layer [1,2], is atomically flat [2,3] and shows electrical conductivity already at submonolayer coverage [4]. The conductance is then well described by a simple Drude model with a mean free path equal to the film thickness [4]. For ultrathin films deposited at room temperature, in contrast, percolation is inhibited by island formation and the conductivity is negligible. Its threshold has recently been measured for different temperatures of deposition and annealing [4]. Conductivity measurements at very low temperatures have manifested an unexpected decrease of the conductivity, and magnetoconductivity studies point to a completely different scattering mechanism [5].

Ag forms initially triangular 2D islands [1], with a close packed (111) arrangement of Ag atoms. The 7 × 7 reconstructed Si substrate is not...
removed by the deposition of Ag, as long as the system is not annealed above 500 K. Above this temperature a phase transition to the $\sqrt{3} \times \sqrt{3}$ phase takes place for a coverage of one monolayer [6]. A recent STM study [7] of the growth of thin Ag films on Si(111) at $T = 150$ K has shown that at low coverage the Ag adatoms form isolated and flat islands with step height of two Ag atoms, which grow laterally with increasing coverage.

In the present work we report a spot profile analysis of low energy electron diffraction (SPA-LEED) study of Ag/Si(111). Such a technique is especially suited for studying heteroepitaxy and allows us to evaluate quantitatively the periodic deviations from an ideal structure, such as the formation of islands, roughness, facets, strain fields and dislocations [8]. Among structural experimental techniques, SPA-LEED is thus unique in giving quantitative information both on periodic structures and on defects, and is complementary to STM, which is more suitable for studying the local topography.

Preliminary discussion on the present investigation was reported in the proceedings of a conference [9].

2. Experimental

The experiment has been performed in ultrahigh vacuum (UHV) at a pressure of $2 \times 10^{-10}$ mbar on an Si(111) single crystal. The sample was prepared in UHV by heating at 1200 °C to remove the oxide protecting layer and was then slowly cooled to room temperature. The system was characterized by energy loss spectroscopy–low energy electron diffraction (ELS–LEED), a technique which allows access to both structural and spectroscopic information [10]. The latter capability was also used in the present experiment to measure the collective electronic excitations in the Ag layers. Such an investigation, reported elsewhere [11], demonstrated that the Ag plasmon is confined inside the single grains, in spite of the metallic conductivity of the film.

The structure of the Si substrate was characterized by SPA-LEED and showed the sharp $7 \times 7$ diffraction pattern characteristic of the reconstructed Si(111) surface. Ag was evaporated from a graphite crucible, heated by electron bombardment, while the crystal was kept either at room temperature or at 100 K. Above this temperature or at 100 K. The amount of evaporated Ag was controlled with a quartz crystal [6]. A recent STM study [7] of the growth of thin Ag films on Si(111) at $T = 150$ K has shown that 1 ML coverage corresponds to one complete Ag layer and is equivalent to $1.5 \times 10^{15}$ atoms cm$^{-2}$.

The spot profile analysis of the LEED spots was performed for the following conditions of deposition temperatures, $T_{deposition}$, thermal treatments and Ag coverages:

- For $T_{deposition} = 100$ K: $H_{Ag} = 1.5, 2.3, 4.5$ and 18 ML.
- For $T_{deposition} = 300$ K: $H_{Ag} = 1.5, 2.3$ and 4.5 ML.

The incident electron energy, $E_i$, was varied in a range between 50 and 80 eV for all the sets of measurements.

3. Data presentation

An example of an Ag/Si(111) LEED pattern is reported in Fig. 1. The data correspond to a deposition of 1.5 ML of Ag at $T = 100$ K, followed by annealing at $T = 300$ K. The broad central spot is indicative of a disordered polycrystalline layer and was then slowly cooled to room temperature. The system was characterized by SPA-LEED and showed the sharp $7 \times 7$ diffraction pattern characteristic of the reconstructed Si(111) surface. The Si(111) 7$\times$7 spots are still visible, while (01) spots of Ag(111) have formed. They are very broad and show an arc shape with a width of some 6°, indicative of rotational disorder.

One-dimensional cuts through the LEED pattern, recorded at $E_i = 55$ eV, are reported in Fig. 2 along the $\langle 11 \bar{2} \rangle$ direction for depositions at $T_{deposition} = 100$ K and for different Ag coverages. With increasing $H_{Ag}$, the intensity of the Si(111) $7 \times 7$ spots decreases while a structured background builds up. Above $H_{Ag} = 2$ ML the (10) peak of Ag(111) appears, while the $7 \times 7$ spots of Si persist up to 3 ML. A broad shoulder
Fig. 1. Two-dimensional LEED pattern for 1 ML Ag/Si(111) 7×7 deposited at 100 K and annealed at 300 K.

grows with coverage under the (00) peak, indicating that the disorder at the surface increases.

The dependence of the SPA-LEED spectra on \( E_i \) is shown in Fig. 3 for \( \theta_{Ag} = 1.5 \) and 3 ML and \( T_{dep} = 100 \) K. In accord with the result of Fig. 2 no diffraction peak associated with the Ag overlayer is present for the lower coverage (it forms only after annealing at 300 K). The (00) spot is very narrow for all \( E_i \) and the Si(111) 7×7 spots are still visible, showing that the layer is still incomplete. For \( \theta_{Ag} = 3 \) ML the (1,0) silicon peak has disappeared, indicating that the Si surface is now totally covered by the Ag layer. The Ag(111) peak is now present as a very broad structure and the (00) spot shows a broad shoulder, which does not vary with energy. On such a shoulder is superimposed a weak peak due to the (1/7,0) spot of the reconstructed Si, whose intensity is also independent of \( E_i \). With increasing \( E_i \) only a general weakening of the intensity of all the peaks related to the Si structure takes place.

In Fig. 4 spot profile analysis is shown for the same films reported in Fig. 3 after an annealing of some minutes at \( T = 300 \) K. As one can see, at \( \theta_{Ag} = 1.5 \) ML the Si spots are still visible and the Ag (10) peak appears, indicating the ordering of the Ag film in (111) oriented islands. At \( \theta_{Ag} = 3 \) ML the Si(10) spot is no longer visible, while the Si (1/7,0) is again still visible on the shoulder of the central peak. The Ag(10) spot is narrower than before annealing, but the profile of the central shoulder is not significantly altered.

In Fig. 5 the behavior with \( E_i \) of the LEED data recorded after room temperature deposition, for \( \theta_{Ag} = 1.5 \) and 3 ML is reported. As one can see the Ag(111) peak is already present for \( \theta_{Ag} = 1.5 \) ML. For \( \theta_{Ag} \leq 3 \) ML, the (10) spot of Si is still visible. It is important to note that for both layer thicknesses the Ag (10) spot is much narrower at higher deposition temperature than for the coldly deposited layer and that the broad and energy-independent shoulder of the (00) spot is not affected by the temperature of deposition and annealing. However, the (00) spot is broader.
ness of the film, which is strictly connected to the
growth mode of the overlayer.

In the present experiment the (10) spot of
Si(111) is visible up to a coverage of about 2 ML
for a deposition temperature of 100 K (see Fig. 2),
indicating that the film is fairly complete, so that
only the transparency of the film for the electrons
provides a minimum intensity of the Si(10) spot.
Annealing the coldly deposited layer to 300 K does
not change the intensity of the Si spots. For Ag
deposition at room temperature, on the contrary,
the (10) spot of Si remains visible with reasonable
intensity up to higher coverages, indicating that
the film did not close up to a thickness of 4 ML.
We infer from this that its grains form separated
islands.

4. Completeness of the film

In the study of the heteroepitaxial growth of
thin films, one important information easily
obtainable by SPA-LEED is about the complete-
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For \( \theta_{Ag} \leq 4 \) ML all the layers, independently of
the deposition temperature, show the Si (1/7 0)
diffraction spot superimposed on the central spike.
As the (10) spot of Si is not visible under these
conditions, we conclude that the presence of the
1/7th order peak is due to a modulation of the Ag
film following the corrugation of the underlying
Si(111)7\times7 structure. This observation is indica-
tive of a relatively flat layer, which is able to follow
the corrugation of the substrate by elastic bending
with an amplitude much less than the layer
distance.
5. Ag grains

The profile of the first-order Ag spot is known to be strongly influenced by the lateral disorder at the surface and its analysis can give quantitative information on the dimension and the orientation of the grains [8]. The full width at half-maximum (FWHM) of the Ag(10) spot indeed provides directly the average grain size, \( d \), which is given approximately by \( d = 2\pi\Delta K / (\Delta K_i = \text{FWHM of the spot}) \) (depending on size distribution). The profile is determined by the incoherent superposition of the waves diffracted from the single grains [12,13] and is independent of \( E_i \). In the present study, the experimental data were fitted by a Lorentzian curve and the FWHM thus obtained was averaged over all the available sets of measurements recorded at different \( E_i \). The values of the average diameter of the grains are reported in Table 1 for different thickness and for different temperature of deposition and annealing.

As one can see, the diameter of the Ag grains increases by a factor of nearly 6 between low and room temperature deposition, even if it cannot yet be strictly correlated to the temperature or coverage, because it also depends on deposition rate, substrate cleanness and annealing time.

As shown in Fig. 1, the Ag spots are not point like, but have an arc-like shape. Heteroepitaxial films sometimes show mosaic structures with small angle misalignment, connected to tilting off the surface normal or to in-plane rotation [8]. The measured spot intensities result then from the incoherent superposition of the reciprocal lattices of all grains. In the case of tilting, an increase of the FWHM of the (00) spot can be observed with increasing \( E_i \), while in-plane rotations do not affect the (00) spot but produce arc-shaped first-order spots. In the present experiment, no energy dependence of the widths was observed, while the (10) Ag spot is arc shaped owing to in-plane misalignment of the grains. The average rotation angle has been calculated from the width of the (10) spot in the azimuthal direction and is found to be 6° ± 0.5° for all coverages and temperatures of deposition, indicating that the orientation of the grains is independent of thickness and of growth mode.

Table 1

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<tr>
<th>( \theta_{\text{Ag}} ) (ML)</th>
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6. Vertical disorder

The broad and intense shoulder under the (00) spot cannot be explained by the lateral disorder of the grains, which is expected to influence only the (10) silver spot. Such a shoulder is present for all temperatures of evaporation and annealing and, as shown in Fig. 2 for the low temperature evaporation case, it increases with coverage.

Stepped surfaces are expected to show a sharp central spike and a shoulder whose intensity varies periodically in opposite phase with energy [14]. Films sometimes show mosaic structures with small angle misalignment, connected to tilting off the surface normal or to in-plane rotation [8]. The measured spot intensities result then from the incoherent superposition of the reciprocal lattices of all grains. In the case of tilting, an increase of the FWHM of the (00) spot can be observed with increasing \( E_i \), while in-plane rotations do not affect the (00) spot but produce arc-shaped first-order spots. In the present experiment, no energy dependence of the widths was observed, while the (10) Ag spot is arc shaped owing to in-plane misalignment of the grains. The average rotation angle has been calculated from the width of the (10) spot in the azimuthal direction and is found to be 6° ± 0.5° for all coverages and temperatures of deposition, indicating that the orientation of the grains is independent of thickness and of growth mode.

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where \( d \) is the vertical distance between two Ag atoms (2.36 Å), \( \theta \) is the incidence angle (6° in the ELS-LEED geometry) and \( S = \Delta \theta / 2\pi \) is an integer for in-phase conditions. Our measurements show on the contrary (see Figs. 2, 3 and 4) that the shoulder is present also for in-phase conditions (e.g. at \( E_i = 60 \text{eV} \), which corresponds to \( S = 3 \)) confirming therefore the presence of some type of morphological or structural surface disorder.

One possibility is the epitaxial roughness of the layer. If present it should give rise to a periodic modulation with \( S \) (or energy \( E_i \)) of the ratio between the integral intensity of the central spike
but does not give rise to a periodicity with \( E_i \). The amplitude of the vertical disorder can be numerically estimated by considering the ratio of the integral intensity of the shoulder to that of the central spike in the in-phase condition \( (E_i = 60 \text{ eV} \text{ in the present case}) \) [15]:

\[
G_0 = \frac{I_{\text{shoulder}}}{I_{\text{spike}} + I_{\text{shoulder}}}
\]

where \( I \) is the integral intensity of the LEED peak. \( G_0 \) is related to the average vertical displacement \( W \) by:

\[
G_0 = \exp\left(-W^2k^2\right)
\]

where \( k \) is the vertical component of the scattering vector.

From this analysis we conclude that \( W \) is in between 5\% and 11\% of the Ag vertical interatomic distance (2.36 Å) and increases slightly with coverage.

The reason of such disorder is that the modulation is caused by nucleation of Ag islands taking place either in the faulted or in the unfaulted halves of the Si(111) \( 7 \times 7 \) unit cell.

### 7. Conclusions

From the spot profile analysis of the LEED pattern of Ag films deposited on Si(111) \( 7 \times 7 \) for different temperatures of deposition and annealing, we conclude that:

1. For deposition at \( T = 100 \text{ K} \), the Ag layer is fairly complete for 1 ML, while for deposition at \( T = 300 \text{ K} \) the layer is formed by separated islands up to coverages of at least 4 ML.
2. The presence of a lateral disorder is demonstrated by the large width of the Ag(10) peak and indicates a mosaic disorder in the Ag layer, with a rotational disorder between the grains and the substrate up to about ±6°.
3. The dimension of the Ag grains increases with the temperature of annealing and deposition, passing from an average value of 1.5 nm for low deposition temperature to 9.5 nm for deposition at 300 K.
4. The broad shoulder of the (00) spot is indicative of a disorder due to grain boundaries producing
a vertical displacement between neighboring grains of the order of 10% of the atomic vertical distance of Ag(111).

5. The presence of the (1/7 0) spot of Si in the shoulder of the central peak indicates a modulation of the Ag film which follows the corrugation of the underlying Si(111)7 × 7 structure. The experiments show that heteroepitaxial films may show some disorder depending on the substrate, the deposition parameters and the annealing conditions. The knowledge of the disorder is needed for interpretation of many other parameters like scattering mechanisms for conductivity, electromigration or for growth phenomena of subsequent layers of different material.

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