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Lattice expansion in islands stabilized by electron confinement: Ag on Si(111)-7×7

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Ag on Si(111)-7×7 was one of the first systems where height selection of metal islands was attributed to electron confinement, i.e., stabilization of selected heights through a quantum size effect (QSE). However, it has been puzzling how the requisite electron standing waves can form, because the Fermi level E_F (along the growth [111] direction) is within the gap for bulk Ag. With detailed experiments over a wide coverage and temperature range, we show that a large increase of 12% is present in the interlayer spacing within the bilayer islands. This can shift E_F below the gap, allowing electron confinement to control height selection. This conclusion is also supported by the observation of a corrugation pattern of period 3 nm on top of the Ag islands, which is bias dependent and can only be the result of QSE-generated standing waves normal to the film.

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Over recent years, strong efforts have been directed toward controlling the epitaxial growth of nanostructures so that growth results in monodispersive particle dimensions. Surprisingly, it was found that using quantum size effects (QSE) (i.e., the dependence of the confined electron energy on island height) provides a robust pathway to select island height on surfaces.[1–11] Islands of near-uniform height can form spontaneously after deposition (i.e., within a few minutes). QSE-selected heights have been observed for soft metals or semimetals deposited on semiconducting substrates. Well-known examples include Ag on GaAs[8] or Pb on Si(111).[2,11] In such systems, it has been determined that two conditions must be satisfied for the QSE to be observed experimentally. First, the "standing" wave condition must be fulfilled. This can be stated as $nd = (\text{odd})\,\boldsymbol{\lambda}_F$, where d is the interlayer spacing, and $\boldsymbol{\lambda}_F$ is the Fermi wavelength. Second, the growth conditions—consisting of surface temperature, deposition flux, and metal coverage—must be favorable, since the uniform-height islands are often metastable.

The growth of Ag(111) on Si(111)-7×7 was one of the early systems[1,12] where preferred heights were observed and attributed to QSE. Supporting this attribution, quantum well states were also observed in photoemission spectroscopy.[13,14] Islands of bilayer height, separated by an inhomogeneous "wetting layer" of Ag, were observed after a specific preparation process. This process consisted of deposition of 1–2 monolayers (ML) of Ag at 150 K, followed by annealing to room temperature.[1,15] This preparation process, compared to a single-step deposition at room temperature,[16,17] is now generally understood to produce a much stronger selection of bilayer islands, i.e., a much narrower height distribution centered at the bilayer height, due to the role of kinetics in bilayer formation in this system. Even taking different preparation techniques into account, however, there are inconsistencies in the literature about whether bilayer growth is sustained past the first Ag bilayer.[1,16,17] One study reports that bilayers are preferred even in Ag islands more than 20-layers high, and even when prepared under the conditions least favorable to bilayer formation, i.e., single-step deposition at room temperature.[17]

At the same time, it has been pointed out that the electronic band structure of bulk Ag in the [111] Γ-L direction exhibits a gap at the Fermi level, E_F.[14,18] Therefore, if the bulk electronic structure of Ag is applicable to surface islands of Ag, there are no free electrons to form standing waves and so QSE cannot be the reason for height selection.

In this paper, we present experiments on Ag/Si(111), which confirm that indeed the two-layer height selection is due to QSE. A large interlayer spacing increase (12% higher than the bulk value) of the first two Ag layers indicates film expansion. Most likely, this causes a downshift of E_F to within the valence band and a concomitant reduction of the energy of the confined electrons within bilayer islands. However, with further Ag deposition the growth mode becomes layer by layer and no other preferred heights are observed; the interlayer spacing in Ag islands larger than two-layers has the normal bulk value. These new measurements and the analysis of the interlayer expansion remove the literature inconsistencies for Ag/Si(111).

Additional evidence that QSE is responsible for height selection is the corrugation pattern on top of flat-topped Ag islands. The period of the corrugation is 3.0 nm, a value close to the period of the 7×7 lattice, which is still present at the Ag-Si interface. The corrugation pattern is a "beating" pattern at the interface well studied also for Pb/Si(111),[19] and it originates from phase variation of the confined electron wave function at the metal/substrate interface. Its existence and its dependence on the tunneling voltage implies a finite $\boldsymbol{\lambda}_F$.[19] The main conclusion of the current work is that it is possible to grow flat top Ag(111) islands with preferred heights on the 7×7 surface because this mixed interface favors interlayer expansion of the first 2 layers.

The experiments were carried out in an ultrahigh vacuum chamber housing a variable-temperature Omicron scanning tunneling microscope (STM) with a typical base pressure of 4.0×10^{-11} mbar; during Ag evaporation the pressure rose to 1.2×10^{-10} mbar or less. A special tip holder allowed for tip

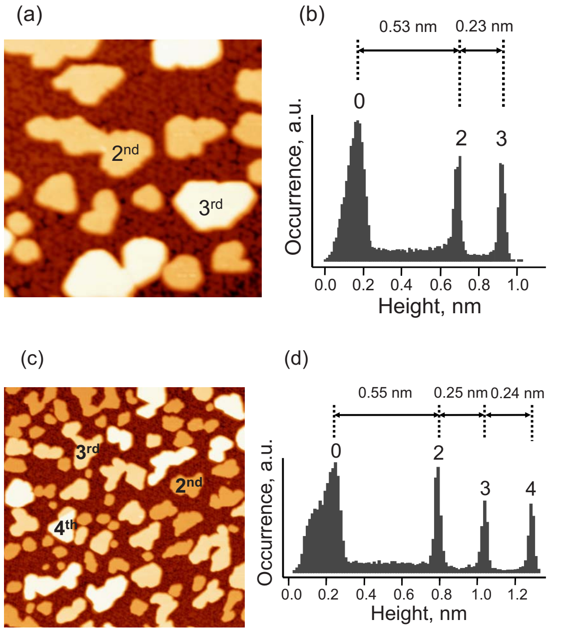

FIG. 1. (Color online) Parts (a) and (c) are STM images taken at +2.0 V bias, in areas of 100 × 100 nm^2 and 250 × 250 nm^2, respectively. Parts (b) and (d) are height histograms corresponding to panels (a) and (c), respectively. In panels a and b, the Ag coverage is 1.2 ML, and in c and d, it is 1.8 ML. The wetting layer is marked as 0 in the height histograms.

cleaning to prepare sharp tips quickly. An Omicron electron beam evaporator was used for Ag deposition. The deposition flux was calibrated from STM images by integrating the volume of Ag islands grown in successive depositions. Temperature was measured from the Omicron temperature calibration plots below and up to room temperature. Above room temperature it was based on the carrier concentration of the Si sample ($10^{18}\ \text{cm}^{-3}$) and the variation of resistivity with T.

Figure 1 consists of representative STM images, and corresponding height histograms, following deposition of Ag at 300 K. Figure 1(a), with a Ag coverage of 1.2 ML, shows mostly two-layer islands plus a few three-layer islands. Figure 1(c), with 1.8 ML, shows a mixture of two, three, and four-layer islands. In Figs. 1(b) and 1(d), the average height of the two-layer islands above the wetting layer is 0.53–0.55 nm. Averaged over a larger region of the surface containing 500 two-layer islands, this value is 0.53 ± 0.03 nm. Sets consisting of 230 and 160 islands are analyzed for the three and four-layer islands, respectively, and the total height for three-layer (four-layer) high islands is found to be 0.76 ± 0.03 nm (1.01 ± 0.03 nm). This corresponds to an average interlayer spacing of 0.25 nm, closer to the bulk value of Ag(111) 0.236 nm. Hence, for the two-layer islands, the interlayer spacing is at least 12% higher than its bulk value (and twice the 0.03 nm uncertainty in the measurement), but for taller islands the average interlayer spacing approaches the bulk value. The robustness of the expansion is also seen in the data of Ref. 1 although this was only shown in the figure without any discussion of its significance.

To eliminate electronic contributions to the measured spacings, the two-layer thickness was measured at different tunneling voltages in the range −2.5 V to +2.5 V. The +2.0 V value represented in Fig. 1 is the lowest measured value. For negative voltage, the spacing increase is even higher, by up to ~20%, so 12% is a conservative estimate.

If there is no in-plane contraction (compressive strain) of the Ag lattice to compensate for the lattice expansion along the surface normal, then the atomic volume of the two-layer islands increases by at least 12% relative to the bulk value. Diffraction studies both with reflection high-energy electron diffraction (RHEED)[20] and low-energy electron diffraction (LEED) show no evidence for lateral contraction. In addition, a 7% contraction of the lateral island dimensions would correspond to a significant change of the observed corrugation period (discussed below) by ~0.2 nm.

A volume increase in a Ag island would lower the electron density, which in turn can possibly place k_F within the valence band. Since E_F is only slightly above the top of the valence band (by ~0.25 eV) a small downward shift in E_F will be sufficient. A simple calculation based on the free electron model with $E_F = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$ (Ref. 21) shows that a 12% increase in volume corresponds to a 8% decrease in E_F (or 0.44 eV larger than 0.25 eV). This simple estimate is only suggestive, since in the real system the volume expansion can also cause sub-bands to shift downwards. However, the final position of k_F (whether within the gap or below the valence band) depends on the relative shift of E_F vs the shift of the top of the valence band. The shift depends also on the effective mass of the sub-band. It is measured with angle-resolved photoemission spectroscopy (ARPES) that for Ag/Si(111) the effective mass is higher for sub-bands closer to E_F,[22] so this will reduce the shift of the top of the valence band more than the shift of E_F and can explain a nonzero k_F. This question requires first principles calculations where the interface structure and the effective mass dependence on sub-band are included.

In any case, the downward shift due to the expansion will lower the total energy of a two-layer film and can partially account for the two-layer stability. In addition the QSE effect due to k_F falling below the valence band would lower the energy even more and stabilize the two-layer islands to a lower energy minimum. Stabilization of 0.2–0.3 eV is quite large compared to the energetic magnitude of the QSE in other systems, where it is estimated to be on the order of a few tens of meV[23,24]—an order of magnitude lower than the values discussed here. This large energy gain is consistent with the high stability observed for the bilayer, where even after annealing to ~400 K (for 15 min) a surface such as that in Fig. 1(a) still exhibits predominantly two-layer islands.

Additional evidence that QSE operates in this system and is responsible for height selection is seen in Fig. 2. Here, the surface was prepared in a two-step process. The main island is one of very few that is laterally large after reaching 300 K, as a result of an unusual fluctuation in the coarsening process. It has an almost-hexagonal shape, indicating that the top layers of the island have the fcc Ag bulk structure. A weak corrugation is seen that has a periodicity of 3.0 nm.

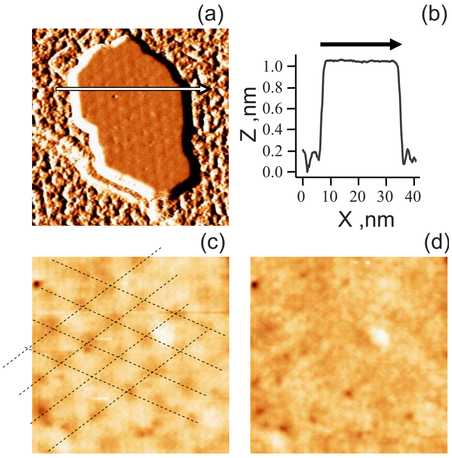

FIG. 2. (Color online) (a) A derivative mode STM image of a surface prepared in a two-step process, $50\times50\ \text{nm}^2$ area, −1.0 V bias, showing a large four-layer island with corrugation on top. (b) Height profile corresponding to the arrow in (a). Parts (c) and (d) are images at −1.0 V and +1.0 V bias, respectively, of the island top shown in (a), with area $16\times17.4\ \text{nm}^2$. Note that the mesh in (c) marks the corrugation.

This "beating" pattern corresponds to $10a_0$, where $a_0=0.29$ nm is the in-plane lattice constant of Ag(111)-(1×1). This is close to the periodicity of the Si(111)-7×7, 2.7 nm. It is known from earlier diffraction experiments[25] that the Ag unit cell is aligned with the Si(111)-7×7 unit cell. In our experiments, the corrugation pattern was studied as a function of the tunneling voltage and found to be bias dependent. Its amplitude was only measurable at negative polarities, indicating that the corrugation is purely electronic. By analogy with the well-studied corrugation on top of Pb/Si islands,[19] a purely electronic corrugation can only originate from "standing waves" normal to the film. These are only possible if $\boldsymbol{\lambda}_F$ exists, i.e., if the Fermi level has moved into the valence band as a result of the interlayer expansion.

In a similar vein, the growth of flat Ag films on Si(111)-7×7 (in the thickness range 3–10 ML) was studied by other authors, using Z-V scanning tunneling spectroscopy, with the tunneling bias voltage V varied up to a value of 10 V.[26] These measurements were sensitive to transmission resonances in the electronic states in the vacuum outside the island. Depending on the energy of the emitted electrons (defined by V) the transition probability of an incident electron wave exhibits transmission maxima that depend on the thickness of the well, and also standing waves that depend on the tip-substrate gap. The interpretation of these spectra require a finite electron density of states at the Fermi level E_F and therefore this further supports the previous conclusion that E_F has dropped into the valence band along the Γ-L direction.

According to our model, the stabilization from QSE would be greatest in the first bilayer, since the Ag lattice relaxes toward the bulk structure for taller islands. Indeed, our experimental data, and some of the data already in the literature, support the conclusion that the first bilayer forms preferentially, but subsequent growth is layer-by-layer. Figure 3 shows the relative areas of n-layer Ag islands as a function of total Ag coverage, prepared by a single-step deposition at room temperature. Clearly, two-layer islands predominate up to 2.4 ML, but at higher coverages three-, four-, and five-layer islands are sequentially populated with equal probability. This is in good agreement with a previous report.[16] These data suggest that growth is not electronic after the first bilayer.

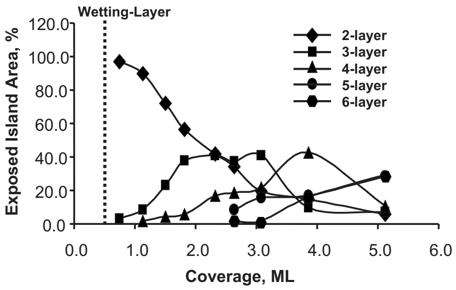

FIG. 3. Relative area of the Ag islands for different heights, as a function of total Ag coverage. Surface is prepared by single-step deposition at 300 K. Diamonds: two-layer islands. Squares: three-layer. Triangles: four-layer. Circles: five-layer. Hexagons: six-layer.

However, the structure of the Ag islands and their surroundings is only partially established, and this contributes some uncertainty to the model for QSE stabilization of the first bilayer. The following facts are known. The islands are surrounded by an inhomogeneous Ag wetting layer. The wetting layer has coverage of 0.5 ML between the Ag islands, wherein regions of high Ag density are interspersed with regions of low density, and the (7×7) unit cell is maintained.[16] The height histograms in Fig. 1 exhibit broad peaks at level 0 because of this rough wetting layer structure. Under conditions where bilayer islands exist, LEED and RHEED patterns both show evidence of unstrained Ag(111), suggesting that the bilayer consists of Ag(111) planes.

The Ag bilayer islands themselves actually consist of 3 layers, since the wetting layer is taken as the point of reference. The third layer is the interfacial layer at the base of the islands, and nominally at the same level as the wetting layer. In this interfacial layer, it is known that the (7×7) periodicity of the Si reconstruction is maintained.[27] The Si occupation at the base is less than 1, indicating that there may be some place exchange between Ag and Si atoms. Our data show that the coverage of Ag contained in the Ag islands (above the wetting layer) varies linearly as a function of deposition time at 300 K, at coverages up to 7 ML, and the intercept on the time axis is found to be 0.50±0.03 ML (from the calibrated flux rate of 0.38 ML/min). This is the Ag coverage in the combined wetting layer and interfacial layer, meaning that the growth of Ag islands does not perturb the total coverage established in the wetting layer. Overall, the evidence to date suggests that the interfacial layer is similar to the wetting layer. However, information about individual atomic positions is not very specific, making it impossible to say whether there is, for instance, rumpling that might propagate into the Ag bilayer above.

In support of our model, a similar, but far more dramatic lattice expansion along the surface normal, was observed during the growth of Al on Si-Al($\sqrt{3}\times\sqrt{3}$) because of QSE.[28]

After a full wetting layer forms, the initial two layers of Al have a total thickness of 0.7 nm, instead of the value 0.46 nm, which would be expected from the normal bulk interlayer spacing. The two layers consist of a dilute and dense layer with a total coverage 1.5 ML and individual heights of 0.35 nm, so the island thickness equals the Fermi wavelength, $\boldsymbol{\lambda}_F = 0.36$ nm, of the Al film. This effect is far more dramatic than that discussed in the current experiments because with the 50% increase of the thickness of the first two layers, the system lowers its electronic energy and attains higher stability, as supported theoretically.[28]

In summary, we have presented new experiments on Ag/Si(111)-7×7, confirming that two-layer islands have special stability with respect to height, and that the origin of the height selection is QSE. Despite the Fermi level being in the gap for bulk Ag along the [111] direction, a large interlayer expansion (12%) normal to the surface shifts the Fermi level below the valance band and can be the reason for the stability. This is supported from the corrugation pattern observed on top of the islands that is a result of the QSE generated "standing waves" normal to the film. Comparison with previous results for Al/Si(111) suggests that volume adjustments to achieve QSE stabilization may be a general phenomenon.

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