Initial Stage of Ag Condensation on Si(111)7×7

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Using scanning tunneling microscopy and spectroscopy we have investigated the growth of a $\frac{1}{3}$-monolayer Ag film on Si(111)7×7 at substrate temperatures of 90 and 130 °C. An Ag-induced subunit has been identified on top of three dangling bonds of the second atomic layer, which may be considered as the critical nucleus of Ag condensation. At 130 °C Ag mostly condenses in the form of triangular-shaped flat islands of equal size, which are preferentially located on faulted halves of the 7×7 unit cells and are explained by a close-packed structure of Ag atoms. On the Ag islands the local density of states near the Fermi level is reduced compared to the uncovered 7×7 unit cells.

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In contrast to numerous investigations of Si(111)$\sqrt{3}\times\sqrt{3}R30°$-Ag [1] not much work has been devoted to the initial stage of Ag condensation on a low-temperature Si(111) substrate. Low means in this context that the substrate temperature is not yet sufficient for the $\sqrt{3}\times\sqrt{3}$ phase transition, which is observed for temperatures above 500 °C and an Ag coverage (Θ) of at least $\frac{1}{3}$ monolayer (ML).[2] Previous studies have already established the *general* nature of the growth process of Ag on Si(111)7×7. Room-temperature deposition leads to a layer-by-layer growth mode up to Θ of a few ML according to the nearly exponential dependency of the Si $L_{2,3}VV$ and Ag M_4VV Auger intensities.[3] For $\Theta=10$ ML, the angle-resolved photoemission results could be explained by the growth of an ordered overlayer structure in the form of Ag(111) domains.[3] Additional information on the general growth process of this system may be inferred from electron microscopic work.[4]

In the present Letter we report on a scanning-tunneling-microscopy (STM) study of the initial stages of Ag film growth on Si(111)7×7. The experiments have been performed at substrate temperatures (T_{sub}) of 90 and 130 °C. As the first step of Ag condensation we have observed ringlike structures on the inner adatoms of both halves of the 7×7 unit cell, which show a triangular distortion and indicate bonding of the Ag atoms to the dangling bonds of the second atomic layer. For $T_{sub}=130$ °C we find that the Ag deposit forms triangular and essentially two-dimensional islands with a close-packed arrangement of Ag atoms. These islands, as well as the subunits, preferentially occupy halves of the 7×7 unit cells where according to the dimer-adatom-stacking-fault (DAS) model[5] a stacking fault is present. On the uncovered parts of the surface we observe the usual 7×7 reconstruction of clean Si(111). The Ag islands still reflect details of the 7×7 reconstruction, which means that the 7×7 structure is preserved on the entire surface. The shape and the size of the Ag islands indicate a very weak or even repulsive interaction of Ag atoms with those substrate sites where according to the DAS structure the dimers of the second atomic Si layer are located. On the Ag islands we observe a reduction of the local density of states both above and below the Fermi level E_F compared with the adatoms of clean Si(111)7×7, which may be understood by a nonmetallic character of the local electronic structure of the Ag islands.

The experimental equipment and technique used for the present results have been described elsewhere.[6,7] We have recorded constant-current topographies (CCT's) for various sample bias voltages U, and current images (CI's). I/U and dI/dU characteristics were determined, which we compare with photoemission results from Ag/Si(111)7×7.[8] As substrates we used p-type (B-doped, 2 Ω cm) Si(111) wafers. Prior to mounting in the microscope, the samples were cleaned in acetone, etched in fluoric acid, and rinsed in methanol and deionized water. *In situ* treatment consisted of degassing and final heat treatment up to 800 °C, until we obtained a clear 7×7 LEED pattern. Ag was evaporated from a quartz-controlled effusion cell at a typical rate of $\frac{1}{90}$ ML/s and at $T_{sub}=90$ and 130 °C. During evaporation the pressure was better than 2×10^{-10} mbar. The present results have been obtained for $\Theta=\frac{1}{3}$ ML, where the 7×7 LEED pattern was weakened but still recognizable. The STM images are shown as gray-tone plots; in the CCT's (CI's) dark parts correspond to depressions (low currents) and bright parts to protrusions (high currents).

In Fig. 1(a) results from Ag/Si(111)7×7 ($T_{sub}=90$ °C) are displayed for an area of $\approx 140\times150$ Å^2. In this image (reflecting the empty states of the sample) many of the atomic subunits are visible, which we believe to be the initial state of Ag condensation. The subunits appear as ringlike structures,[9] where the edges consist of oblong protrusions and the center shows a triangular depression. The inner adatoms of the 7×7 unit-cell halves are incorporated in the subunit, while the corner adatoms are not affected. As an atomic model for the observed subunits we propose that Ag atoms are bonded to the inner adatoms *and* the dangling bonds of the second

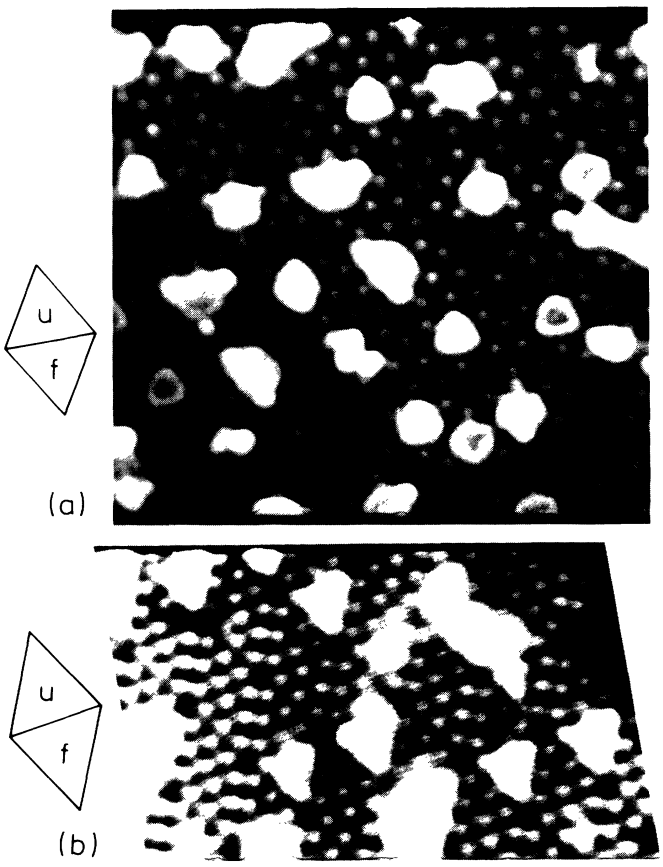

FIG. 1. CCT from $\frac{1}{3}$-Ml Ag on Si(111)7×7 obtained at (a) $U=2$ V, $I=3$ nA, $T_{sub}=90\,^{\circ}C$ and (b) $U=2$ V, $I=2$ nA, $T_{sub}=130\,^{\circ}C$. The faulted and unfaulted halves are labeled f and u, respectively. The area of (b) is $\approx 110\times180$ Å^2.

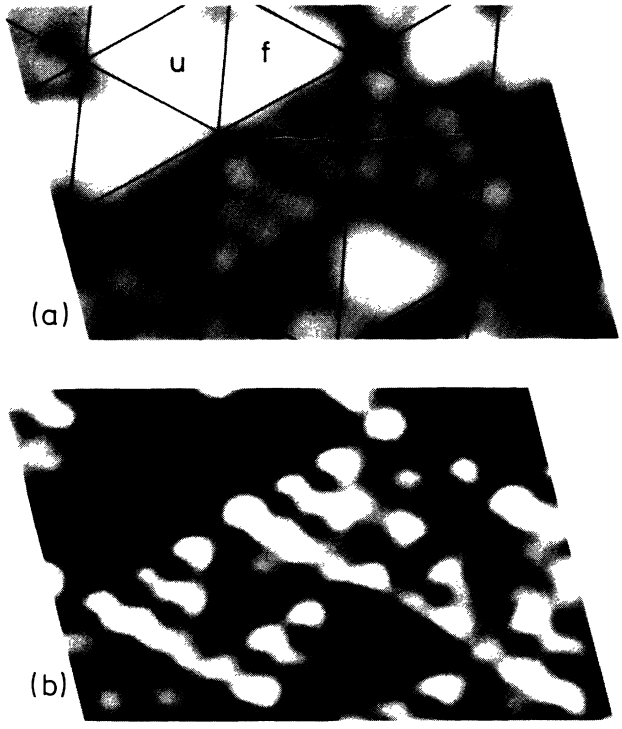

FIG. 2. (a) CCT acquired simultaneously with CI's at $U=-2$ V and $I=4$ nA. (b) CI obtained at $U=0.5$ V.

atomic layer of the DAS structure. The first step of Ag condensation therefore consists of saturation of these dangling bonds, which means that the ringlike structures would contain at least six Ag atoms. Since only a negligible number of smaller Ag-induced features could be identified in the CCT's these subunits represent the critical nuclei for Ag condensation, which continues by the addition of further Ag atoms until the 7×7 unit-cell half is covered completely. Several not yet completed triangular Ag islands are visible in Fig. 1(a).

For $T_{sub}=130\,^{\circ}C$ the Ag deposit mostly forms such triangular islands on top of 7×7 reconstructed Si [Fig. 1(b)]. The subunits frequently visible for $T_{sub}=90\,^{\circ}C$ are not present on the CCT displayed in Fig. 1(b) but are sometimes also detected for deposition at $T_{sub}=130\,^{\circ}C$. The surface area covered by the triangular Ag islands is exactly the same as would be expected for $\Theta=\frac{1}{3}$ ML and a condensation into a two-dimensional close-packed structure. According to this analysis each completed island would contain 36 Ag atoms.[10] The average height of these islands is 0.5–1 Å above the adatoms of the 7×7 unit cells for *both* polarities of the sample bias voltage. An examination of their surfaces shows that in some cases the underlying adatom structure is still visible [see Fig. 1(a)]. The triangles are preferentially located on top of the faulted halves of the 7×7 unit cells [see also Fig. 1(a)].

To find an explanation for the structural behavior, we have measured CI's simultaneously with a CCT under the condition of a fixed sample-tip distance.[11] Representative results are collected in Fig. 2. The lateral resolution attained was worse than in the results shown above; nevertheless, the CCT clearly shows the 7×7 adatom pattern and triangular Ag islands [Fig. 2(a)]. Since a negative stabilization voltage has been employed (i.e., tunneling from occupied states of the sample into empty tip states), the faulted half of the 7×7 unit cell is distinctly higher than the unfaulted half, leading to the well-known threefold symmetry of the adatom pattern in this case.[12]

For a sample bias voltage of 0.5 V corresponding to tunneling into unoccupied states of the sample, the positions of the Ag islands appear as dark areas in the CI [Fig. 2(b)]. The same behavior is found for a CI measured at -0.5 V (not shown here). Qualitatively, a small tunneling current is associated with a low density of states. Compared with uncovered 7×7 unit cells the formation of the Ag islands is therefore connected with a reduction of the density of states at least 0.5 eV below and above E_F. It has to be noted that the adatom posi-

tions of clean Si(111) are characterized by metalliclike surface states, which already at small sample bias lead to an appreciable tunneling current.[7,11]

This remarkable observation is supported by an analysis of local I/U [Fig. 3(a)] and dI/dU [Fig. 3(b)] characteristics and photoemission results from a room-temperature-deposited Ag film on Si(111)7×7 [Fig. 3(c)]. The tunneling current on the Ag islands is extremely small for $-0.5\ \mathrm{V} \leq U \leq 1\ \mathrm{V}$, while I from the Si adatoms rises already for small U and therefore delivers the dominant contribution to the CI. The same information is contained in the dI/dU's, which in the same range of U are much smaller on the Ag islands than on the adatom positions. We note for the adatom positions the occurrence of a maximum in dI/dU for ≈ -1 V, which previously was assigned to a local density-of-states maximum on the dangling-bond positions of the second atomic layer of Si(111)7×7.[7,11] The same tendency of reduction of the density of states below E_F and the disappearance of the metalliclike edge of clean Si(111)-7×7 upon Ag deposition ($\Theta = \frac{1}{3}$ ML) is seen in Fig. 3(c), where photoemission results from clean and Ag-covered Si(111)7×7 (Ref. 8) are reproduced.[13] In our opinion, the reduction of density of states near E_F and the lack of metalliclike behavior on the Ag islands is quite surprising and probably a consequence of appreciable Ag/Si interaction. The possibility that the I/U's of the Ag islands are affected by the properties of a local Schottky barrier[14] also has to be considered for a full understanding of the I/U characteristics.

Details of the interaction between the Ag atoms and the Si substrate may be derived from the shape of the Ag islands, whose edges essentially agree with the positions of the dimers in the DAS model. In other words, the dimer sites are not occupied by the Ag atoms in the initial stage of condensation as a result of repulsive interaction. As a matter of fact, with increasing Θ (and at 130 °C) the system continues two-dimensional growth and does not yet start the formation of three-dimensional Ag clusters which are observed at higher temperatures.[15] This may be seen in Figs. 1(b) and 2(a), where neighboring halves of 7×7 unit cells are covered in some cases. The preferential growth of Ag islands on the faulted halves does not find its expression in the I/U characteristics, which did not show significant differences for islands grown on faulted or unfaulted halves.[16]

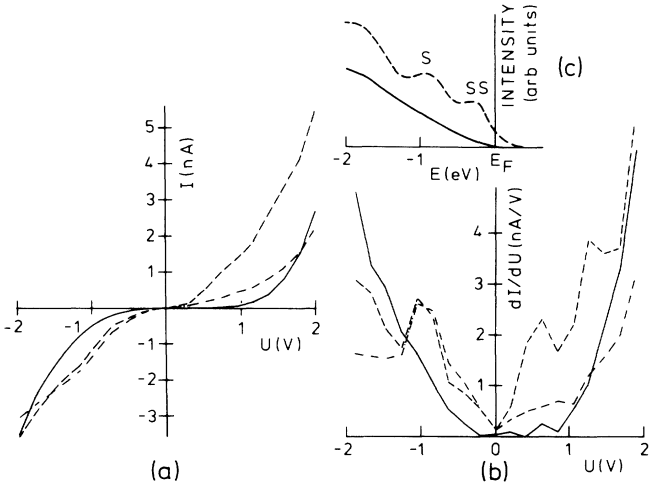

FIG. 3. (a) I/U and (b) dI/dU characteristics of the data shown in Fig. 2. The dashed (dash-dotted) lines have been obtained for the adatom positions of the unfaulted (faulted) half, and the full lines for Ag-covered parts. (c) Angle-resolved photoemission ($\hbar\omega = 21.22$ eV) from clean (dashed line) and Ag-covered ($\Theta = \frac{1}{3}$ ML; full line) Si(111)7×7 at a polar angle of 15° in the $[\bar{1}\bar{1}2]$ azimuth, which has been chosen for optimum intensity of the metalliclike surface state SS (Ref. 8).

The reduction of the density of states on the Ag islands partly explains why the height difference seen by the tip on the scanning of covered and uncovered parts of the surface is much smaller than expected for the size of the Ag atoms[17] and under the assumption of Ag atop positions. A closer proximity between tip and sample is needed on the Ag islands to reach the value of I set in the feedback circuit of the system. However, a slight incorporation of Ag atoms in the very rough surface of 7×7-reconstructed Si(111) may also contribute to the observed small height of the Ag islands. Because of this roughness the Ag islands cannot be completely flat as is actually observed, e.g., in Fig. 1(a). We emphasize that a regular pattern (eventually related to a close-packed structure of metal atoms) could not be detected on top of the islands. This is not surprising since the detection of an atomic corrugation on a close-packed metal surface has turned out to be difficult and could only be achieved under specific conditions of the STM experiment.[18] Since the image shown in Fig. 1(a) has been acquired under optimum operation parameters as may be deduced from the low noise of the 7×7 pattern, we conclude that the observed lack of fine structure and the smoothness is not caused by instrumental limitations and therefore supports our assignment of the Ag islands as due to a close-packed structure. We note that a rectangular two-dimensional pattern recently observed by Ganz, Sattler, and Clarke on the systems Ag and Au on graphite[19] cannot account for the triangular shape of the islands that we observe on Ag/Si(111)7×7.

In conclusion, we have shown that STM provides very detailed information on the Ag/Si interaction in the initial stage of Ag deposition. We have observed Ag-induced atomic subunits, which are assigned to the critical nuclei of two-dimensional island growth of Ag. The shape of the Ag islands in the submonolayer range is essentially determined by the underlying 7×7 reconstructed Si(111), which is not changed by deposition of $\frac{1}{3}$-ML Ag at $T_{sub} \leq 130$ °C.

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tronic (Burghausen) for providing us with the Si wafers.

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[2]The values given here correspond to experimental conditions where, according to our experience, a well developed $\sqrt{3}\times\sqrt{3}$ structure may be observed by scanning tunneling microscopy on parts of the surface.

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[9]We note that in case of negative sample bias the subunits appear at approximately the same height level as a more triangular structure with three lobes pointing into the direction of the inner adatoms. The differences seen for both polarities of U may be attributed to the formation of bonding and antibonding states in the subunits.

[10]The exact agreement between the surface area covered by triangles and the expectation due to a close-packed structure is regarded as somewhat fortuitous, since the determination of areas on STM images is dependent on the chosen contrast, the accuracy of the evaporation rate (approximately 5%), and density variations of the islands over the surface.

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[17]The diameter of Ag atoms in bulk Ag is 2.98 Å [C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976)].

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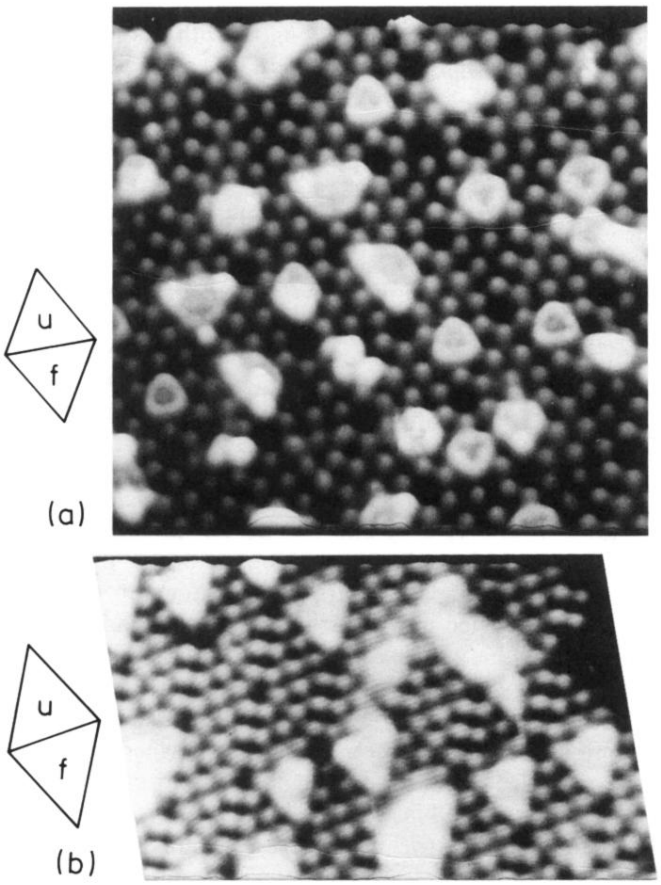
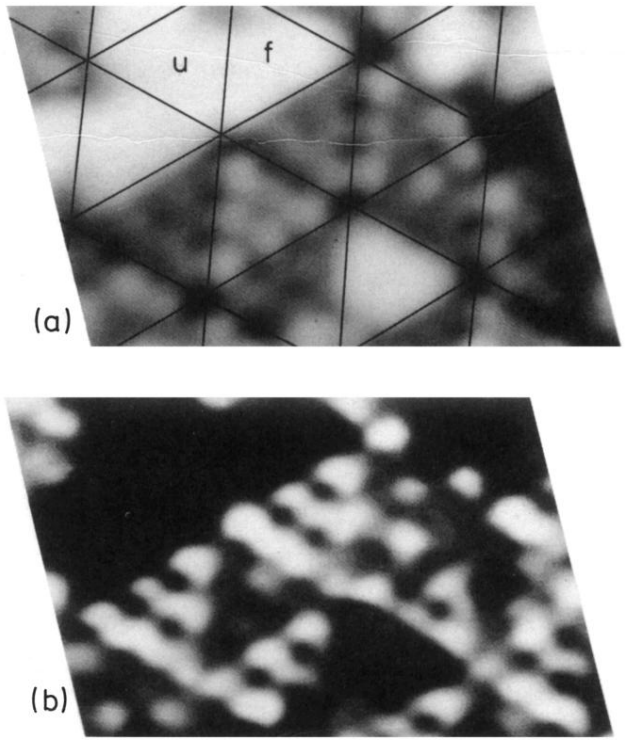


FIG. 1. CCT from $\frac{1}{3}$-Ml Ag on Si(111)7×7 obtained at (a) $U=2$ V, $I=3$ nA, $T_{sub}=90\,^{\circ}C$ and (b) $U=2$ V, $I=2$ nA, $T_{sub}=130\,^{\circ}C$. The faulted and unfaulted halves are labeled f and u, respectively. The area of (b) is $\approx 110\times180$ Å^2.



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