Surfactant-Induced Layer-by-Layer Growth of Ag on Ag(111): Origins and Side Effects

J. Vrijmoeth,[1,*] H. A. van der Vegt,[2] J. A. Meyer,[1] E. Vlieg,[2] and R. J. Behm[1]
[1]*Abteilung Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm, Germany*
[2]*Foundation for Fundamental Research on Matter–Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*

(Received 24 February 1994)

It has been shown that submonolayer deposits of Sb change the growth mode of Ag(111) from multilayer to layer-by-layer. Using scanning tunneling microscopy, we identify the two main origins of this behavior. (i) Sb lowers the mobility of Ag adatoms on terraces *and* growing islands. As a direct consequence, the *additional* edge barrier (barrier to descend a step minus surface diffusion barrier) is reduced. (ii) Sb lowers the mobility along step edges, inducing dendritic island shapes. Both effects favor smoother growth. Neither a lower Ag surface mobility nor heterogeneous nucleation are sufficient for a smooth growth.

PACS numbers: 68.55.–a, 61.16.Ch

The mechanisms underlying epitaxial growth have been extensively studied over the past few years. While first work has concentrated on clean surfaces, the effect of adsorbates ("surfactants") on the morphology has been included recently [1, 2]. These studies have revealed that the film morphology obtained is strongly dependent on the kinetics of intra- and interlayer mass transport, more specifically, on whether or not the material deposited on top of a growing two-dimensional island can reach its edge and fall down, so that the growing layer is completed before the next one starts to grow [3–5].

In a recent x-ray diffraction study, a striking change in growth behavior of Ag was observed for going from clean to Sb-precovered Ag(111) [6]. No layer-by-layer growth behavior is observed for Ag on clean Ag(111) over the whole temperature range studied, between 575 and 175 K. Rather the growth gradually changes from step flow to multilayer growth with several layers simultaneously exposed: The reflected x-ray intensity is constant at 575 K and shows a continuous decay at lower temperatures. In contrast, on a surface precovered with 0.2 monolayer (ML) of Sb, a layer-by-layer growth behavior is observed at temperatures between 225 and 375 K. This is evident from periodic oscillations in the reflected intensity which die out only after ~25 ML of Ag have been deposited. Hence, Sb acts as a "surfactant." These findings were tentatively explained by proposing a repulsive barrier for Ag adatoms to move over descending step edges on the clean surface, which would impede interlayer Ag mass transport. It was suggested that this barrier is reduced due to the Sb being adsorbed at the island edges and that thereby interlayer Ag transport becomes more efficient. From the steep initial decay in the reflected intensity it was concluded that Sb adatoms also act as nucleation centers for Ag islands.

This peculiar growth behavior has motivated further work. Oppo, Fiorentini, and Scheffler [7] found in *ab initio* calculations that Ag is more strongly bound on Ag than on Sb. From this they suggested that the mobility of Ag adatoms should be reduced in the vicinity of Sb and that the resulting increased Ag island density would cause the transition to layer-by-layer growth. That proposal contradicts other available data. Not layer-by-layer, but instead multilayer growth along with increased island densities due to slower diffusion is observed for going to lower temperatures [5, 6]. Thus, an increased island density due to a lower Ag mobility alone [7] is insufficient for explaining the smoother growth.

On the other hand, Rosenfeld *et al.* have shown that the growth on Ag(111) may be forced to become (quasi) layer-by-layer if the island density is enhanced artificially by heterogeneous nucleation. In order to descend from an island, the adatoms deposited on top may have to try several times to move over the edge barrier. Reducing the island dimensions *without reducing the adatom mobility on top* results in an enhanced attempt frequency of adatoms visiting the step edges and thus an enhanced interlayer transport [5]. These authors speculated that the smooth growth on Ag(111) would be analogously induced by an increased island density in the presence of Sb, due to a reduction of the Ag surface mobility on the substrate layer only. It was proposed that the Sb would only move up to the next growing layer upon coalescence of the former so that the mobility on top of the islands would not be reduced. The same picture was supported by Tersoff, Denier van der Gon, and Tromp [8].

To settle the issue of the Sb-induced transition to layer-by-layer growth, we have studied the growth mechanisms using scanning tunneling microscopy (STM). In the present Letter, we show that none of the models put forward correctly describes how Sb affects the growth on Ag(111). We find that the Sb-induced change in morphology has two origins. (i) Sb slows down the Ag adatom mobility *both* on the substrate layer *and* on top of the growing islands. The increased surface diffusion barrier directly affects the additional energy barrier at the step edge, defined as the diffusion barrier at descending step edges minus the surface diffusion barrier, and induces the smooth growth.

0031-9007/94/72(24)/3843(4)$06.00

(ii) Sb slows down the adatom diffusion along step edges. This gives rise to irregular, dendritic, island shapes and induces a further enhancement of the interlayer transport. We find that heterogeneous nucleation [5,6] is important for the first growing Ag layer only. It is not responsible for the observed continuous oscillations.

The STM experiments were performed in a UHV system operating at pressures $<1 \times 10^{-8}$ Pa. The Ag sample was cleaned by repeated sputter and anneal cycles (600 and 700 K) and prolonged high temperature treatments (1000 K, 10 h) to obtain an almost perfect surface with large terraces up to 1 μm in size. The surface was chemically clean as judged by Auger electron spectra. STM data show that less than 10^{-5} of the surface was covered by contaminants. Ag and Sb were deposited with rates of $\sim$1 ML per min. The pressure rise during evaporation was lower than 1×10^{-8} Pa. During evaporation and STM imaging the sample was held at room temperature.

In agreement with the earlier work [6,9], we observe multilayer growth for Ag on clean Ag(111), with the evolution of growth "pyramids" (Fig. 1). After deposition of 0.25 ML of Ag, compact islands have developed with an average island-island distance of about $\sim$3500 Å, which indicates a large mobility of Ag adatoms on the terraces and along the island edges (not shown). Second-layer nucleation is seen at coverages of 0.6 ML [Fig. 1(a)], well before coalescence of the first-layer islands. After deposition of 2.7 ML of Ag [Fig. 1(b)] four layers are found to be exposed simultaneously. Finally, at a coverage of 25 ML, at least 17 layers are left open [Fig. 1(c)]. The early onset of second-layer nucleation is direct evidence for the presence of an additional barrier for diffusion over the step edges, so that interlayer mass transport is hindered.

Sb adsorbed on Ag(111) at room temperature induces a dramatic change in growth behavior of Ag. The Sb is identified either as small depressions of $\sim$1 Å depth, the latter depending on the tunneling conditions and tip state (the depressions may even show up as protrusions), or as small islands with a height of close to one layer and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. As concluded from the calibration of the Sb source, there is one Sb atom per $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell. Direct counting reveals that the depressions also contain a single embedded Sb atom each, in agreement with calculations [7]. With 0.08 ML of Sb preadsorbed, the density of Ag islands grown in the first layer has increased by 3 orders of magnitude as compared to that on the clean surface [Fig. 2(a)]. Closer inspection reveals the islands have not formed by homogeneous nucleation, but are attached to the perimeter of the protruding $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands, which act as nucleation centers. Thus two-dimensional growth is expected and indeed observed in the first layer [Fig. 2(b)].

Growth at Ag coverages exceeding 1 ML also proceeds in a layer-by-layer fashion, but with a much smaller island density than that observed in the first layer. Figure 2(c) shows the film after deposition of 1.7 ML of Ag. Only three third-layer islands are present on the image although the second-layer islands have already partly coalesced. The irregularly structured perimeter of these islands is reminiscent of dendritic growth. These characteristics are maintained at larger coverages. Films of 4.6 and 9.1 ML (not shown) have only three layers exposed, and the Ag islands exhibit relaxed dendritic shapes. In films thicker than 1 ML no evidence for the protruding

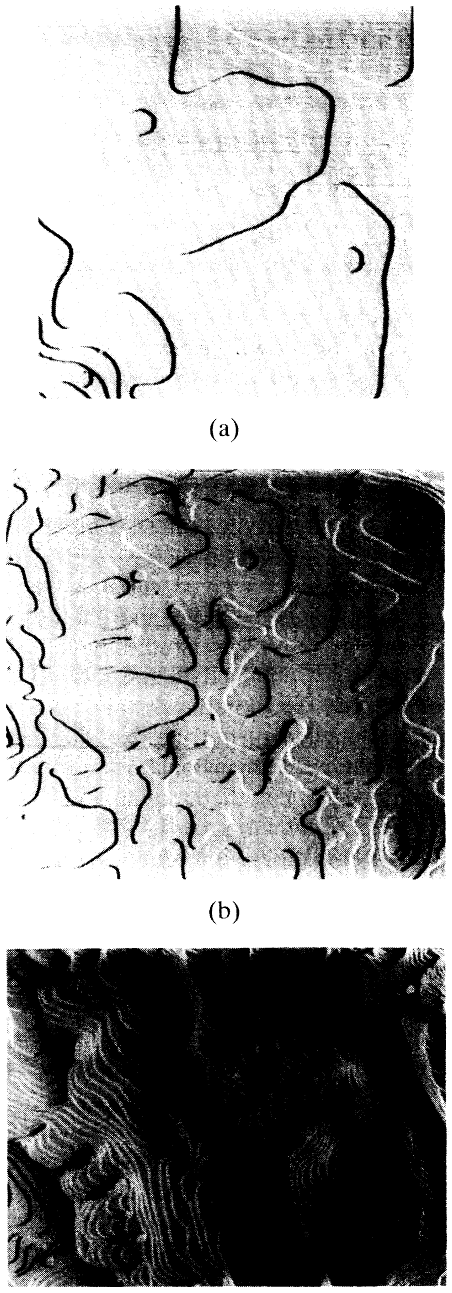
(a)
(b)
(c)

FIG. 1. Homoepitaxy of Ag(111) observed with STM. A multilayer growth behavior is observed. Nominal film thicknesses: (a) 0.6, (b) 2.7, and (c) 25 ML. Fields of view: (a) 7500×7500, (b) $11\,000 \times 11\,000$, and (c) $11\,000 \times 9500$ Å^2.

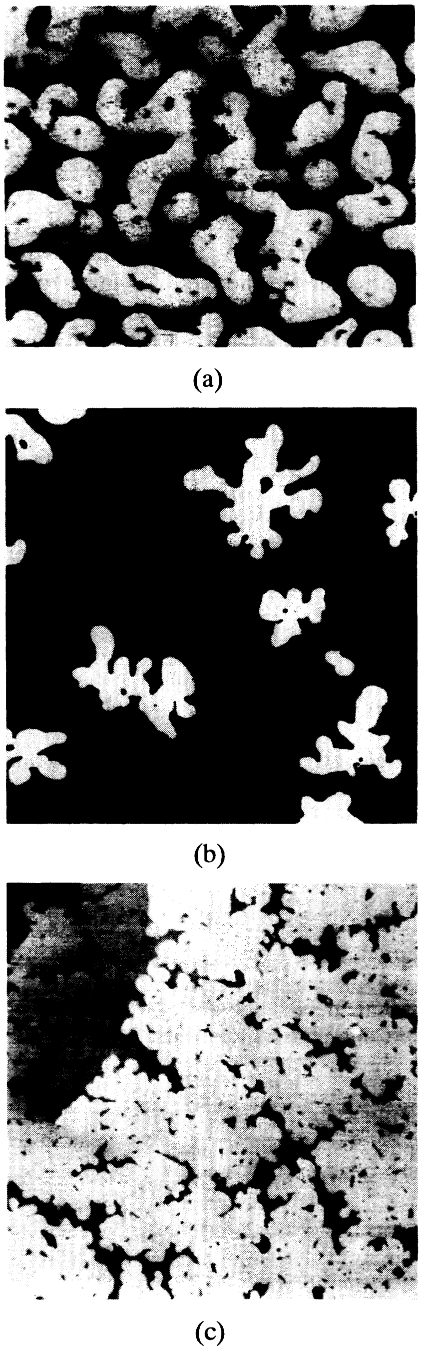

FIG. 2. Growth of Ag on Sb-precovered Ag(111) observed with STM. A layer-by-layer growth behavior is induced. The Sb precoverage is 0.08 ML. Ag coverages: (a) 0.5, (b) 1.1, and (c) 1.7 ML. Fields of view: (a) 2500 × 2200, (b) 4800 × 4500, and (c) 5700 × 5700 Å^2.

$(\sqrt{3} \times \sqrt{3})R30^\circ$ islands is found and only embedded Sb atoms are observed in the surface, *both in the terraces and in the islands*. Thus, the embedded Sb atoms segregate to the top. Auger electron spectroscopy analysis reveals, however, that the Sb surface concentration decreases slowly with increasing thickness of the Ag film, i.e., part of the Sb atoms are incorporated in the growing film [10].

The fact that the growth in higher layers also proceeds in a layer-by-layer fashion suggests that nucleation by the $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands is *not* decisive for the Sb-induced change in growth behavior and that the segregating Sb atoms play a role in the growth kinetics as well. This is confirmed by an experiment in which the Sb-precovered surface ($\Theta_{\mathrm{Sb}} \sim 0.08$ ML) was annealed to 470 K before Ag deposition. As a result of the annealing, all $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands are fully converted into individual embedded Sb atoms. Hence, these are more stable, in agreement with calculations [7]. Deposition of 0.13 ML of Ag on such a surface yields an island density much smaller than on the unannealed surface, but still higher by a factor of 6 as compared to clean Ag(111), indicative of a lower surface mobility of Ag adatoms on the terraces, rather than heterogeneous island nucleation by embedded Sb [10]. In addition, the Ag islands again have irregular (quasi-) dendritic island shapes (not shown). We attribute these shapes to a reduced Ag adatom mobility along the island edge due to the coadsorbed Sb (diffusion limited aggregation) [11, 12]. Again, continued Ag growth proceeds in a layer-by-layer fashion, and again we observe Sb atoms embedded both in the terraces and in the growing islands.

The Ag adatom surface mobility strongly depends on the concentration of embedded Sb atoms. We have deposited various coverages of Sb, annealed the surface to produce the embedded Sb, and subsequently deposited Ag. As a result, we find that the Ag island density increases by a factor of 10^3 as the Sb precoverage is increased from 0 to 0.3 ML. That increase in island density can plausibly be explained assuming an increase in diffusion barrier E_d by about 0.5 eV [10]. During growth the Sb surface concentration decreases steadily with increasing film thickness leading to a slowly decreasing island density.

The growth behavior as observed by STM is completely consistent with the earlier findings by van der Vegt *et al.* [6]. We find that the smooth growth of Ag(111) occurs along with a reduced mobility of Ag adatoms by Sb (i) on the surface and (ii) along the step edges. These two modes of mobility reduction induce the smooth growth as follows.

(i) A reduction of the surface mobility is comparable to what happens upon lowering the temperature. It favors multilayer growth if an effective diffusion barrier exists for adatoms to move over the island edges [3, 5, 6, 13]. Thus, a smooth growth is expected only if the barrier for interlayer transport at the edges *is* reduced by Sb. In this context, the *additional* edge diffusion barrier Δb is decisive, defined as the diffusion barrier at descending step edges E_b minus the surface diffusion barrier E_d [see Fig. 3(a)].

The increased surface diffusion barrier E_d directly causes a reduction of the additional barrier Δb at the edge (Fig. 3): In order to maintain an additional barrier the edge barrier E_b would have to show a similar increase. The observation of a smoother morphology suggests that the additional barrier decreases or vanishes upon Sb preadsorption [Fig. 3(b)]. *The latter can thus*

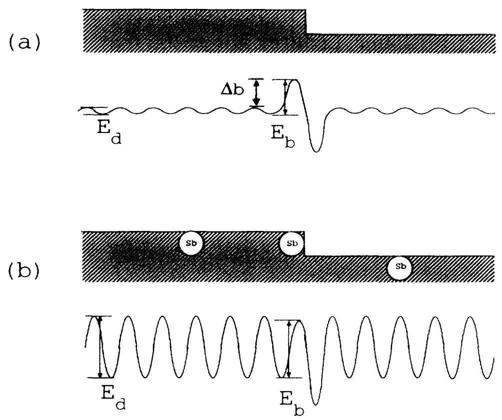

FIG. 3. Schematic diagram of the surface diffusion potentials governing interlayer transport. (a) A diffusion barrier E_b at the step edge, which represents a significant additional barrier $\Delta b = E_b - E_d$, limits interlayer transport and induces a multilayer growth behavior. (b) An increased diffusion potential makes Δb decrease or vanish and layer-by-layer growth prevails.

be induced by the increased surface diffusion barrier alone. A reduction of the total edge barrier E_b by Sb adsorbed directly at the steps, as proposed originally [6], is not required to explain the data. The adsorbed Sb may possibly even *increase* the absolute edge barrier E_b.

For completeness, we note that the reduced surface mobility of Ag adatoms further favors the smooth growth in another way. The Ag mobility is lowest in the first layer and increases with film thickness due to partial incorporation of Sb. This results in an additional, but weak contribution to smoother growth [10].

(ii) The reduced mobility *along island edges* induces dendritic island shapes [11]. This results in enhanced edge lengths and hence the attempt frequency of Ag adatoms visiting the island edges for descent is increased. As a result, the interlayer transport is further enhanced [13, 14]. In addition, one may speculate that kinks, which occur in large concentrations in the irregular edges, have lower edge barriers and hence allow adatoms to descend more easily. This would contribute to the effective reduction of the additional barrier at the step edges (i).

We finally note that the qualitative picture derived from the data is fully corroborated by a quantitative analysis. Details of our model will be presented in a forthcoming paper [15]. Here, we give relevant results. The multilayer growth of clean Ag(111) is properly described assuming an additional barrier Δb for an adatom to descend step edges which amounts to 150 ± 30 meV. We find that the smooth growth upon Sb adsorption cannot be explained on the basis of the dendritic island shapes (ii) alone. The additional barrier at the edge Δb must be reduced with respect to that on clean Ag(111). For instance, at a Sb precoverage of 0.08 ML the additional barrier must have deceased by more than 30 meV in order to account for the layer-by-layer growth [15].

Recently, Esch *et al.* have shown that in the case of Pt/Pt(111) an O-induced smoothening of the growth is similarly due to a lowering of what they call the barrier height for adatom motion across step edges [16]. Our analysis reveals that such lowering, i.e., of the *additional* barrier, does not need to occur via a reduction of the absolute barrier by direct O adsorption at the edges. It is already accounted for by the increased surface diffusion barrier [15], as for Ag/Sb/Ag(111).

In summary, the transition to smooth growth of Ag(111) originates from an Sb-induced lowering of mobility of Ag adatoms on the terraces and along island edges. The *additional* barrier for adatoms to descend a step edge is lowered through the surface diffusion barrier. Embedded Sb efficiently moves up into the growing islands.

We gratefully acknowledge fellowships from the Alexander von Humbolt Foundation (J. V. and J. A. M.). Part of this work was supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) through the Stichting voor Fundamental Onderzoek der Materie (FOM).

---

*Present address: Department of Applied Physics, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

[1] D. A. Steigerwald, I. Jacob, and W. F. Egelhoff, Jr., Surf. Sci. **202**, 472 (1988).
[2] M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[3] R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **65**, 733 (1990).
[4] R. Q. Hwang, C. Günther, J. Schröder, S. Günther, E. Kopatzki, and R. J. Behm, J. Vac. Sci. Technol. A **10**, 1970 (1992).
[5] G. Rosenfeld, R. Servaty, C. Teichert, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **71**, 895 (1993).
[6] H. A. van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg, and J. M. C. Thorton, Phys. Rev. Lett. **68**, 3335 (1992).
[7] S. Oppo, V. Fiorentini, and M. Scheffler, Phys. Rev. Lett. **71**, 2437 (1993).
[8] J. Tersoff, A. W. Denier van der Gon, and R. M. Tromp, Phys. Rev. Lett. **72**, 266 (1994).
[9] K. Meinel, M. Klaua, and H. Bethge, Phys. Status Solidi (a) **110**, 189 (1988).
[10] H. A. van der Vegt, J. A. Meyer, J. Vrijmoeth, R. J. Behm, and E. Vlieg (to be published).
[11] R. Q. Hwang, J. Schröder, C. Günther, and R. J. Behm, Phys. Rev. Lett. **67**, 3279 (1991).
[12] T. A. Witten and L. M. Sanders, Phys. Rev. Lett. **47**, 1400 (1981).
[13] C. Günther, S. Günther, E. Kopatzki, R. Q. Hwang, J. Schröder, J. Vrijmoeth, and R. J. Behm, Ber. Bunsenges. Phys. Chem. **97**, 522 (1993).
[14] M. Bott, T. Michely, and G. Comsa, Surf. Sci. **272**, 161 (1992).
[15] J. A. Meyer, J. Vrijmoeth, H. A. van der Vegt, E. Vlieg, and R. J. Behm (to be published).
[16] S. Esch, M. Hohage, T. Michely, and G. Comsa, Phys. Rev. Lett. **72**, 518 (1994).

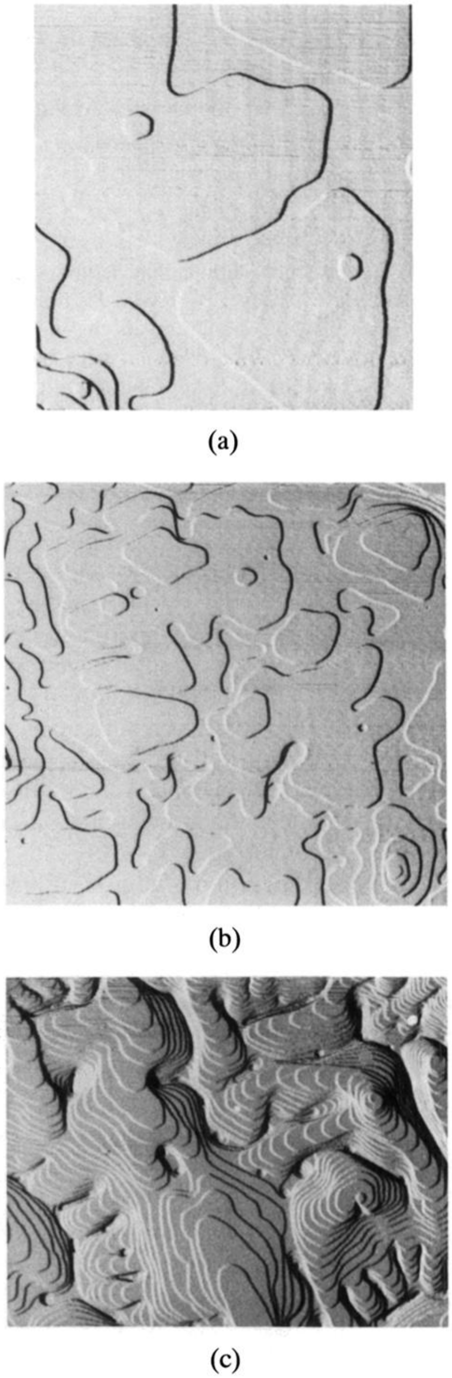

FIG. 1. Homoepitaxy of Ag(111) observed with STM. A multilayer growth behavior is observed. Nominal film thicknesses: (a) 0.6, (b) 2.7, and (c) 25 ML. Fields of view: (a) 7500×7500, (b) $11\,000 \times 11\,000$, and (c) $11\,000 \times 9500$ Å^2.

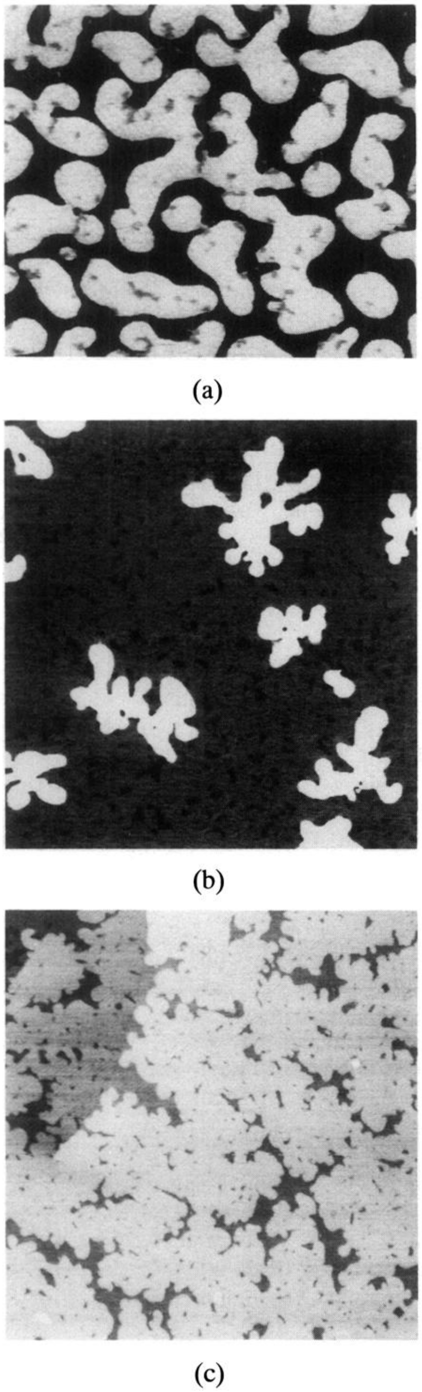

FIG. 2. Growth of Ag on Sb-precovered Ag(111) observed with STM. A layer-by-layer growth behavior is induced. The Sb precoverage is 0.08 ML. Ag coverages: (a) 0.5, (b) 1.1, and (c) 1.7 ML. Fields of view: (a) 2500 × 2200, (b) 4800 × 4500, and (c) 5700 × 5700 Å^2.