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Sb-enhanced nucleation in the homoepitaxial growth of Ag(111)

H. A. van der Vegt*
FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

J. Vrijmoeth
Abteilung Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm, Germany
and Department of Applied Physics and Materials Science Centre, University of Groningen Nijenborgh 4,
9747 AG Groningen, The Netherlands

R. J. Behm
Abteilung Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm, Germany

E. Vlieg
FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

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The effect of Sb on the homoepitaxial growth mode of a Ag(111) surface has been studied by scanning tunneling microscopy. In a previous paper we reported on the effect of Sb on the interlayer diffusion barrier of Ag(111). Here we describe in more detail the effect of Sb on the island nucleation and surface diffusion. We find a homogeneous effect of the Sb on the Ag(111) surface, while heterogeneous nucleation and sticking can be excluded. The surface diffusion barrier appears to be linearly dependent on the Sb concentration. This shows that Sb has an effect not only locally at the step edges, but also on the terraces where it decreases the mobility of the Ag atoms. Further, we show that the Sb segregates efficiently during growth.
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I. INTRODUCTION

In a previous x-ray-diffraction study[1] we showed that the deposition of small amounts of Sb can change the growth mode of Ag(111) from three-dimensional into layer-by-layer. Using scanning tunneling microscopy (STM)[2] we found that the main origin of the change in growth mode is a decrease of the additional diffusion barrier at step edges that hinders atoms to descend at step edges (Ehrlich-Schwoebel barrier).[3–5] In addition, the interlayer transport is increased by the dendritic island shape and the partial incorporation of the Sb during growth, but these effects were shown to be small.

Because the Ehrlich-Schwoebel barrier E_a is the difference between the total barrier at the step E_b and the barrier for diffusion on the terrace E_d ($E_a=E_b-E_d$), the decrease of the Ehrlich-Schwoebel barrier can be caused by either a decrease of the total barrier at the edge E_b or by an increase of the surface diffusion barrier E_d (see Fig. 1). We have shown that the latter is the case for the Ag growth with Sb,[2] which implies that the main effect of the Sb is not local at the step edge.

In this paper we will describe in more detail the effect of Sb on the nucleation of the Ag islands and on the surface diffusion on the terrace. Furthermore, we present the results of an Auger electron spectroscopy (AES) study that shows that the Sb segregates efficiently during the growth.

II. EXPERIMENT

The experiment was performed in an ultrahigh vacuum system operating at pressures $<10^{-8}$ Pa. The Ag(111) single crystal was cleaned by repeated sputter (600 K) and anneal (700 K) cycles and prolonged high-temperature treatments (1000 K for 10 h) to obtain a surface with terraces up to 1 μm in size. The surface was chemically clean according to the Auger electron spectra. The STM images show that less than 10^{-5} of the surface was covered by contaminants.

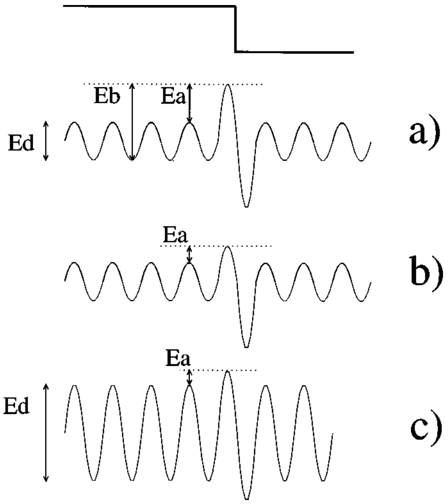

FIG. 1. Schematic surface potential at a step edge with an Ehrlich-Schwoebel barrier. The Ehrlich-Schwoebel barrier on the clean surface (a) can be decreased in two ways: (b) by a local decrease of the total barrier at the step or (c) by a global increase of the surface diffusion barrier. E_d denotes the surface diffusion barrier, E_b the total barrier at the edge, and E_a the additional (Ehrlich-Schwoebel) barrier.

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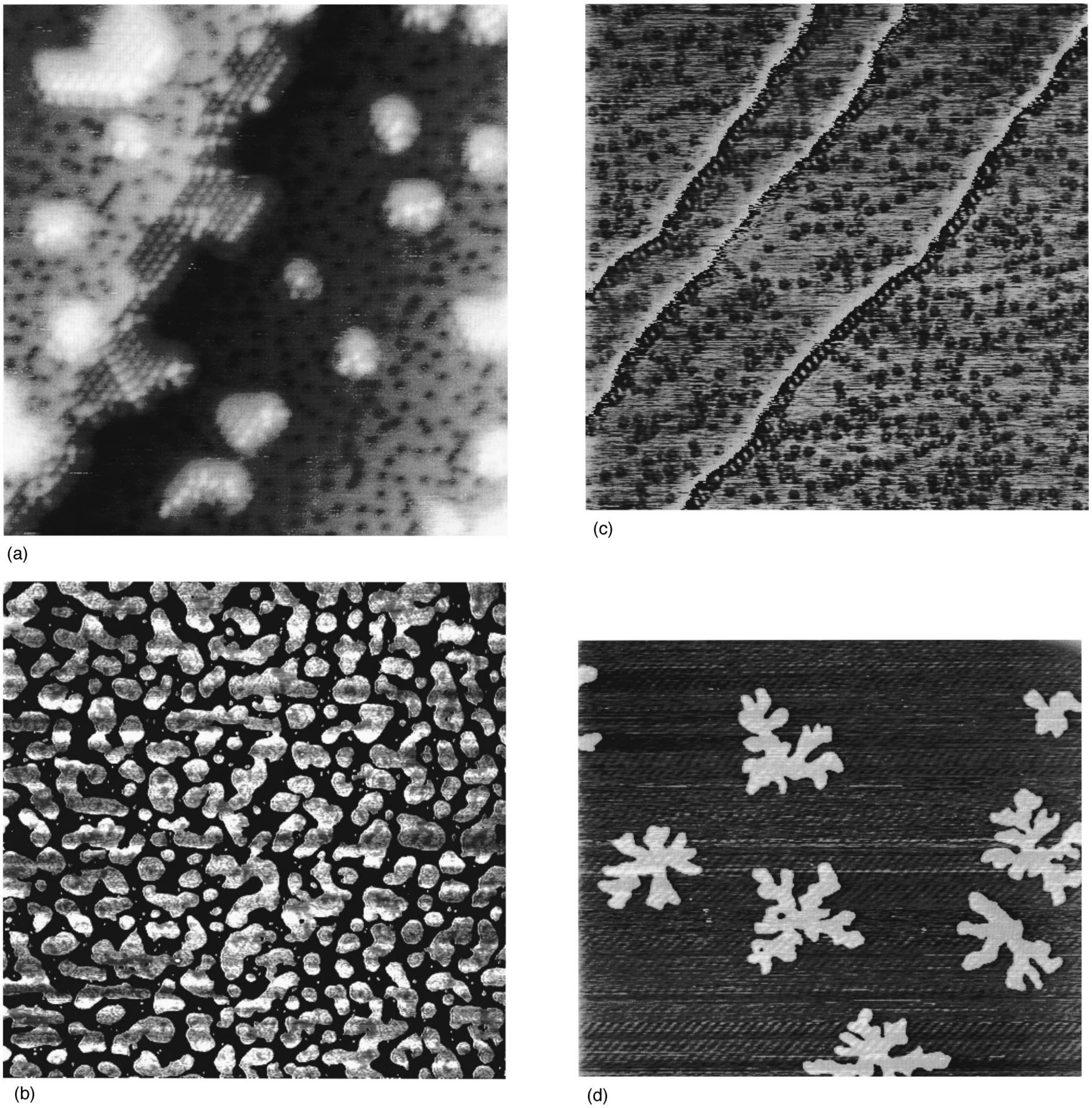


FIG. 2. A series of STM images showing the influence of an annealing treatment on the subsequent Ag growth. (a) 0.12 ML Sb on clean surface; 22 nm×23 nm, (b) 0.08 ML Sb+0.5 ML Ag, 400 nm×400 nm, (c) 0.08 ML Sb annealed, 30 nm×25 nm, (d) 0.08 ML Sb annealed +0.13 ML Ag, 600 nm×500 nm.

Ag was evaporated by heating a Ag droplet positioned in a coiled tungsten basket. Sb was deposited from a Knudsen cell with water cooling. The deposition rate was in both cases approximately 1 ML/min and the pressure during evaporation was below 10^{-8} Pa. The deposition and imaging were done with the substrate at room temperature.

III. ANTIMONY-INDUCED ISLAND NUCLEATION

A. Sb position and growth morphology

In Ref. 2 we discussed STM results showing the effect of predeposited Sb on the growth of Ag(111). Figure 2 shows in more detail the difference between as-deposited and annealed Sb on the growth of the first monolayer of Ag. The first image [Fig. 2(a)] shows the surface after 0.12 ML Sb deposition. The Sb atoms are present at the surface in two different forms. Part of the Sb is sitting on top of the surface and at step edges in ordered clusters with a $(\sqrt{3}\times\sqrt{3})R30°$ superstructure[6] (Sb clusters are white in this image). The rest of the Sb is embedded in the surface, shown as dark ‘‘holes’’ in the image. If on such a surface Ag is deposited, the Sb islands act as nucleation centers, see Fig. 2(b). Due to the contrast between the Sb (dark gray) and Ag (light gray) atoms, we see that no Ag islands without Sb are formed. From the second layer on, the Sb is always embedded *in* the top layer, no heterogeneous nucleation occurs, and the islands grow with a dendritic shape.[2,7]

When an Sb precovered surface is annealed ($\sim$0.1 ML Sb, 475 K for 10 min) we find that the Sb clusters are dissolved in the top layer of the surface [Fig. 2(c)] and no ordered Sb clusters or single Sb atoms are present on top of the surface. The embedded position is thus the equilibrium position, which is in agreement with *ab initio* calculations.[8] We also see that all the step edges are covered with Sb atoms. When we deposit Ag on this surface, we observe the dendritic morphology already in the first layer [Fig. 2(d)], as in the higher layers of the growth without annealing. This indicates that the heterogeneous nucleation around the Sb clusters in the first layer is a special case that is not essential for the induced layer-by-layer growth.

B. The nucleation mechanism

Since it is the Sb in embedded form that causes the change in growth mode in the higher layers, we have used surfaces with annealed Sb to study the nucleation mechanism in more detail. In order to relate the amount of embedded Sb to the density of Ag islands we deposited various amounts of Sb and subsequently annealed these surfaces (10 min at 475 K). In this way we obtained surfaces with different concentrations of embedded Sb atoms. On the annealed surfaces we then deposited Ag (Fig. 3) and determined the density of the Ag islands. The result of this experiment is given in Fig. 4. We see that the island density increases exponentially with the amount θ of Sb. In the following, we will discuss different mechanisms that could increase the nucleation density.

According to standard theory for homogeneous nucleation[9] the island density at a given coverage outside the transient region is given as function of deposition rate and diffusion constant by

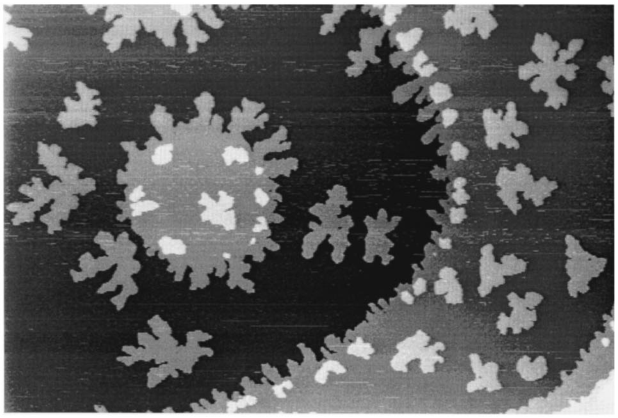
$$N \propto (R/D)^{i/(i+2)}, \tag{1}$$

with R the deposition rate, $D = D_0 e^{-E_d/kT}$ the diffusion constant, and i the critical nucleus size. Since the deposition rate was not varied and the critical nucleus size is not expected to change, the Sb must affect the diffusion constant. If we assume that Ag adatoms have a larger probability to stick to embedded Sb atoms than to the Ag substrate atoms, the island density should increase only linearly with Sb coverage (for low coverages) in contrast with our observation. Geometrical site blocking is another way to increase the island density. The Sb atoms could exclude a number of sites that cannot be occupied by Ag atoms. This can be considered as an increase of the effective deposition rate because there are fewer sites available for the arriving atoms. The increase of the deposition rate will be linear with the amount of Sb. Another effect of site blocking is that, assuming a random walk of the Ag atoms, the average time to walk from one position to another is longer because a number of pathways is blocked by the Sb atoms. This reduces the diffusion constant linearly with the amount of Sb. So the joint effect on the deposition rate and on the diffusion constant cannot account for the observed exponential increase in island density.

The simplest explanation for the experimental relation $\ln(N) \propto \theta$ is to assume that the diffusion barrier E_d increases linearly with the Sb coverage. This is a surprising result since it means that all sites experience a reduction in diffusion constant. Using Eq. (1) with $i = 1$, the best fit to the data is obtained for

$$E_d = E_{d0} + 1.7\theta \tag{2}$$

with E_{d0} the diffusion barrier on the clean surface and the energies given in eV. This fit is shown in Fig. 4 as the solid line. From this expression it follows that the barrier for surface diffusion has increased by $\sim$520 meV in case of 0.3 ML annealed Sb, assuming a critical nucleus size $i = 1$. A lower limit for the change in the barrier is obtained when we calculate the barrier for $i = \infty$ which yields 170 meV. It is not clear what the critical nucleus size at room temperature is. Up to 200 K it has been shown that $i = 1$,[10,11] at room temperature the same value has been assumed.[12] The derived change in diffusion barrier can be compared with the available values for the surface diffusion barrier for the clean


(a)

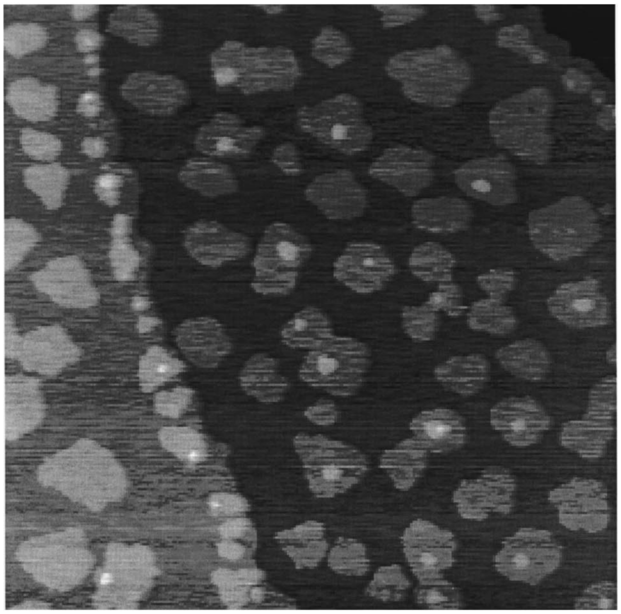

(b)

FIG. 3. STM images of the Ag island density as a function of the Sb predosing. (a) 0.15 ML Sb annealed $+0.36$ ML Ag, 95 nm$\times$60 nm, (b) 0.3 ML Sb annealed $+0.3$ ML Ag, 15 nm$\times$15 nm.

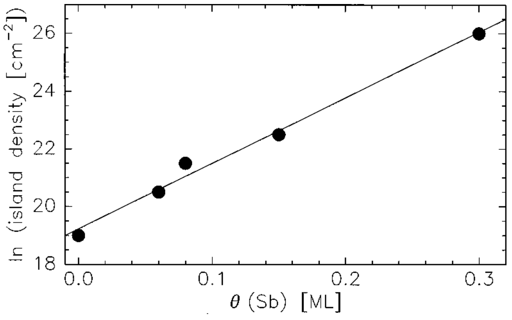


FIG. 4. The natural logarithm of the Ag island density as a function of the amount of predeposited, annealed Sb. The solid line is a fit using Eq. (2), see text. The Ag coverages for which the island densities were determined were 0.5 ML for Sb coverages of 0.06 and 0.08, 0.36 ML Ag for an Sb coverage of 0.15 ML, and 0.3 ML Ag for an Sb coverage of 0.3 ML.

Ag(111) surface: 60–120 meV (Refs. 13–15) found by calculations and 100–180 meV (Refs. 10 and 11) determined experimentally. The change in diffusion barrier as given by Eq. (2) is plotted versus the amount of Sb in Fig. 5.

In a previous paper,[16] we derived a method to calculate the Ehrlich-Schwoebel barrier from the measured island sizes and interisland distances, and found a value of 150 meV for the clean surface. Smilauer and Harris[17] used a similar method, using slightly different assumptions, and derived a value around 200 meV. Since our conclusions do not depend on the exact values, we will, in the following, continue to use the method from Ref. 16. Using this, also the effective Ehrlich-Schwoebel barrier in the case of an Sb precovered surface can be estimated. For 0.08 ML Sb we find $E_a = 125$ meV and for 0.3 ML Sb, $E_a = 12$ meV. Since we now know both E_a and the change in surface diffusion barrier E_d, the change in the total barrier at the step edge can be calculated using $E_b = E_d + E_a$. The results of these calculations are shown in Fig. 5. We see that even though *the total barrier at the step edge increases, the Ehrlich-Schwoebel barrier decreases because the surface diffusion barrier increases even more*. The Sb has a global effect and the picture of an Sb atom attached to the step edge reducing the barrier locally [Fig. 1(b)], is therefore not valid.

The observation of the second-layer nucleation in an early stage for Ag deposition on the surface with 0.3 ML annealed Sb [Fig. 3(b)] also supports the idea that the effect of Sb is not local. If the only effect of Sb would be to lower the barrier at a step edge, it is expected that a larger Sb concentration yields a smoother growth. However, when the main effect of the Sb is to lower the mobility on the terraces and so indirectly reduce the additional barrier at the step edge, the second-layer nucleation can be explained. In this case of 0.3 ML Sb coverage the mobility on the surface is reduced to the extent that atoms deposited on top of islands will not be able to reach the island edges before more atoms have arrived and the critical nucleation density is exceeded. The Ehrlich-Schwoebel barrier has decreased almost to zero (12 meV), but this decrease is not enough to prevent nucleation with the given reduced surface mobility. This clearly shows that both the height of the Ehrlich-Schwoebel barrier and the mobility on the surface determine the growth mode.[16] The early second-layer nucleation also shows that 0.3 ML Sb is too much for smooth growth. The optimum amount of Sb lies between 0.1 and 0.2 ML.

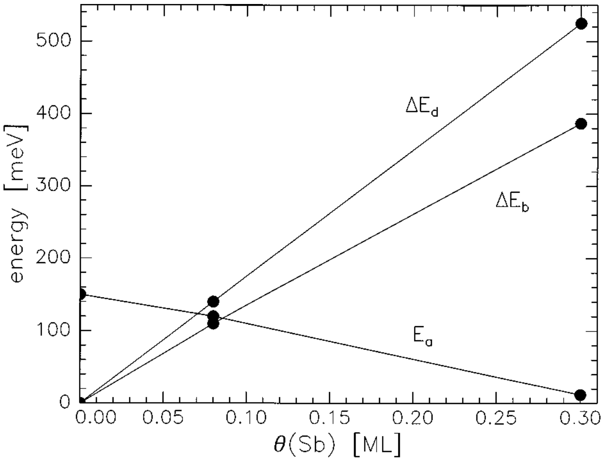


FIG. 5. Surface diffusion barriers as a function of the amount of predeposited, annealed Sb. E_a is the additional barrier at a step edge, ΔE_d is the change in the activation barrier for surface diffusion and ΔE_b is the change in the total barrier at a step edge; ΔE_d and ΔE_b are given with respect to the values for a clean surface.

Recently, Markov[18] proposed an alternative effect of surfactants. He suggested that the surfactant is attached to the step edge and instead of lowering the Ehrlich-Schwoebel barrier, it hinders atoms arriving from the low side to attach to the step. This mechanism, however, cannot explain the occurrence of second-layer nuclei on top of small islands, as observed for larger annealed Sb amounts (Fig. 3).

Liu *et al.* recently showed[19] that the diffusivity of the Ag adatoms on the terrace is reduced when the Sb atoms act as repulsive impurities, as proposed by Oppo, Fiorentini, and Scheffler.[8] In this case the repulsion is not only present at the step edges, as Markov[18] proposed, but everywhere on the terrace. The simple scaling relation [Eq. (1)] has then to be replaced by a more complicated one. It was shown that for a repulsive action extending up to three lattice sites away from the impurity, the island density can increase to values comparable to the values found in our experiment. This agrees with our conclusion that Sb affects the diffusion on the terrace in a nonlocal way. For an Sb coverage of 0.3 ML, the average distance between two Sb atoms is approximately $1/\sqrt{(0.3)} = 1.8$ lattice constants. Therefore, all Ag atoms on the terrace will experience the repulsion of the Sb atoms and at all positions the diffusion constant has decreased. In our experiment, we find the change of the effective diffusion constant. It is clear that in case of the repulsive Sb atoms, not all positions on the surface are equivalent and that the diffusivity changes with the actual distance to the surrounding Sb atoms. This point requires further investigation, since it is not clear that the theory of Liu *et al.* yields the relation $\ln(N) \propto \theta$ over the full range investigated here.

IV. THE SEGREGATION OF Sb

The observation of many intensity oscillations in the x-ray-diffraction experiment already showed that the segregation of Sb is quite efficient, because only on the starting

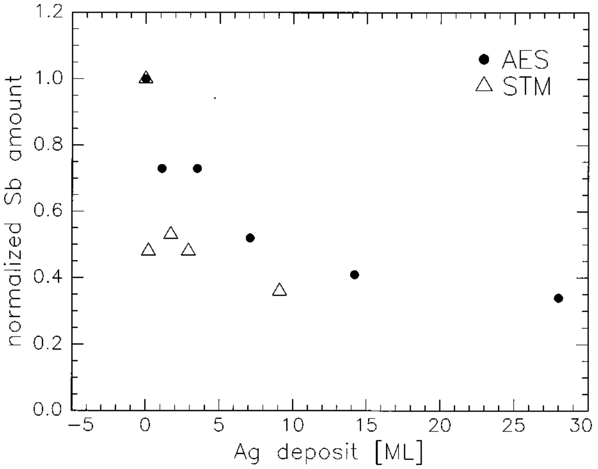


FIG. 6. The amount of Sb at the surface determined by AES (solid circles) and STM (triangles) as a function of the amount of subsequently deposited Ag. The amount of Sb is normalized to the value before Ag was added (0.5 ML for AES, 0.08 ML for STM).

surface a small amount of Sb was deposited.[1] Intensity oscillations were observed from 225 to 375 K, indicating that the segregation is not very sensitive to the temperature. In order to investigate the segregation of Sb during growth quantitatively, we have performed AES. First we deposited 0.5 ML of Sb on the clean substrate and subsequently we measured the intensities of the Ag and Sb Auger peaks as a function of Ag deposition. The result is shown in Fig. 6. We see that the Sb segregation is rather efficient: after 15 ML of Ag deposition, the Sb peak has reduced to 40% of the original intensity. This implies an Sb incorporation of ~5% for each ML of Ag deposition.

We also counted the Sb atoms visible on the STM images at different stages of the growth, for a precoverage of 0.08 ML Sb (as deposited). The Sb concentrations determined in this way are also shown in Fig. 6. From both methods it follows that incorporation is largest during deposition of the first Ag layer, but that after this, the Sb concentration is only slowly decreasing. It could well be that in the first layer extra Sb is left behind at defects present at the starting surface.[20] The systematic higher amount of Sb detected with AES can be explained by the larger probing depth of this technique. When the embedded Sb is covered by Ag, a place exchange mechanism puts the Sb again in the top layer.[7] *Ab initio* calculations indeed find that incorporation of Sb in the first layer has a lower energy than in the second layer.[8] On the basis of the efficient segregation one can conclude that the mobility of the Ag adatoms is hardly affected by the decreasing Sb concentration.[16]

V. CONCLUSIONS

In conclusion, we have shown that heterogeneous nucleation occurs only during growth of the first layer and is not essential for the change in growth mode. The main effect of Sb is an increase in the surface diffusion barrier of Ag, leading to a concomitant reduction of the additional step edge diffusion barrier. We showed that the effect of Sb on the diffusivity on the terrace cannot be explained by site blocking or sticking and therefore, the effect must extend farther than the nearest-neighbor sites. This agrees with a recent proposal of a repelling action of embedded Sb atoms extending to three lattice units away from the Sb atoms. Further we showed that the segregation of Sb during growth is very efficient. Therefore, only a small amount of Sb on the starting surface is needed for a long lasting effect on the growth mode. The optimum amount of Sb is 0.1–0.2 ML.

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*Present address: Philips Semiconductors, Gerstweg 2, 6534 AE Nijmegen, The Netherlands.

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