Layer-by-Layer Growth of Ag on Ag(111) Induced by Enhanced Nucleation: A Model Study for Surfactant-Mediated Growth

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It has been reported that the growth mode of Ag on Ag(111), which is usually multilayer (3D), changes to layer-by-layer (2D) growth if Sb is used as a surfactant. In a model study on the clean system Ag/Ag(111) (without any surfactant) we find that two-dimensional layers do grow, if the substrate is prepared with an anomalously high density of Ag nuclei. As an enhanced density of nuclei is also observed in the presence of Sb, this effect may explain the mechanism for surfactant-induced layer-by-layer growth.

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Although surfactant-mediated epitaxial growth has attracted increasing interest in recent years, only little is known about the actual reason for the change in growth mode under the influence of a surfactant. For heteroepitaxial systems, a change in growth mode has been attributed to a change in surface free energies of substrate and film [1–3]. However, typical growth experiments are performed far from equilibrium, so that the equilibrium concept of surface free energies might be inappropriate and kinetic effects need to be accounted for. For instance, reduced surface diffusion in the presence of surfactants appears to play an important role in the observed changes in growth mode [4,5].

In order to achieve a better understanding of surfactant-induced changes in growth kinetics, it is worthwhile to study a homoepitaxial system, for which the appearance of different growth modes is due to kinetic effects alone. The decisive process, which controls the growth modes in homoepitaxy, is the mass transport between layers (interlayer mass transport). Efficient interlayer mass transport is necessary for layer-by-layer (2D) growth: In the ideal case, one layer is completely filled before nucleation and growth in the next layer starts and, therefore, atoms that are deposited on top of existing 2D islands have to be able to descend from these islands and fill the lowest level layer. If, however, interlayer mass transport is hindered, growth in the next layer starts before the previous one is filled and 3D structures develop (multilayer or 3D growth).

The interlayer mass transport has been described in terms of an activation barrier for the downward diffusion of adatoms at island edges [6,7]. Within this picture, it is attractive to relate a surfactant-induced change from multilayer to layer-by-layer growth to a direct influence of the surfactant on the activation barrier: Surfactant atoms diffuse to the island edges and locally alter the energetics in a way that the activation barrier for interlayer mass transport is reduced. Recently, this process was proposed by van der Vegt *et al.* as an explanation for their results on the growth of Ag on Ag(111) after deposition of 0.2 ML (monolayer) Sb onto the substrate [8]. Whereas multilayer growth was observed for all studied substrate temperatures in the absence of Sb, layer-by-layer growth resulted in the presence of Sb on the substrate. However, a direct influence on the activation barrier is not the only possible cause for enhanced interlayer mass transport. In this Letter we demonstrate that an artificially high density of nuclei, as observed in many studies of surfactant-mediated growth and also by van der Vegt *et al.*, induces enhanced interlayer mass transport leading to layer-by-layer growth. Our demonstration is done for the *pure* Ag/Ag(111) system in order to separate this effect from any further influence of a surfactant.

The experiments are performed in a UHV molecular beam scattering apparatus described in detail elsewhere [9]. The silver crystal was prepared in UHV by sputtering and heating cycles after having removed the disordered layer of about 2 μm resulting from the polishing of the crystal by low energy argon ion sputtering. This procedure resulted in a mean terrace width of more than 1000 Å. Ag is deposited onto the crystal using a home-built sublimator. Information on the growth mode is obtained by monitoring the specular peak height I of the reflected He beam during deposition of Ag onto the sample. The angle of incidence is chosen to $\vartheta_i = 73°$, corresponding to out-of-phase conditions. As in reflection high energy electron diffraction, oscillations in the specular peak height indicate layer-by-layer growth, i.e., efficient mass transport between layers, whereas a monotonic decay of the signal is observed for multilayer growth.

Prior to a growth experiment the substrate is prepared with a high density of Ag nuclei by two different methods. The first one makes use of the temperature dependence of the density of nuclei. It is well established that under usual conditions, the density of two-dimensional nuclei formed during a deposition experiment increases with increasing supersaturation, i.e., with decreasing substrate temperature at fixed deposition rate (or with increasing deposition rate at fixed substrate tem-

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perature). Deviations from this behavior have been observed for Pt/Pt(111) at high temperatures [10], but as we have checked, the system Ag/Ag(111) behaves completely normally in this respect. Therefore an artificially high density of nuclei (i.e., a density higher than that characteristic for the given growth temperature T_g) can be prepared by depositing a few percent of a monolayer at a temperature T_p *lower* than T_g. The temperature is then raised to T_g and the deposition is started [11].

In order to make this procedure work it has to be checked that during heating to T_g, the density of nuclei is not reduced by coarsening effects (Ostwald ripening). This can be done by an annealing experiment as shown in Fig. 1. Here, a certain number of nuclei (or small islands) has been grown by depositing 0.1 ML of Ag onto the substrate at a temperature of 100 K. Subsequently, the substrate is heated at a constant rate of 1 K/s while monitoring the specular peak height. Corrected for Debye-Waller effects, the data obtained in this manner are plotted as a function of the temperature in Fig. 1. Between 100 and 200 K, the intensity hardly changes indicating that no structural changes occur. Above 200 K, the intensity increases to reach a plateau between 240 and 300 K and above 300 K a rapid increase in intensity is observed until the initial value ($I/I_0=1$) is reached. The rapid increase can easily be attributed to the onset of Ostwald ripening: Islands decompose by two-dimensional evaporation of adatoms which accommodate at steps (or very few large islands). The first annealing step is attributed to a change in island shape from irregular ("fractal") to compact. Such a rearrangement of atoms without changing the island density results in an increase of the He specular intensity because the number of edge atoms that give rise to diffuse scattering is reduced. Indeed, scanning tunneling microscopy (STM) investigations of the system Pt/Pt(111) reveal the existence of fractal islands at low temperatures and a transition to compact island shapes at a temperature well below the temperature needed for the thermal creation of adatoms [12]. Scaling these results to the Ag(111) surface, one obtains a good agreement with the observed temperature dependence. Therefore we conclude that heating to a temperature below 300 K does not significantly affect the island density. Having established this, we can now proceed with the actual growth experiments.

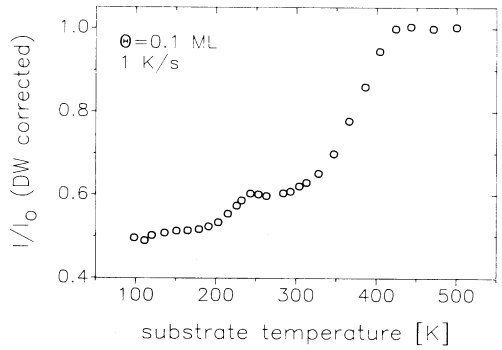

FIG. 1. Evolution of the normalized He specular peak height as a function of substrate temperature during heating at a constant rate of 1 K/s, after having deposited 0.1 ML of Ag at a substrate temperature of 100 K. The intensity is normalized to the temperature dependent reflectivity of the bare substrate (Debye-Waller curve).

A typical example for a set of growth experiments is shown in Fig. 2. All curves are obtained under identical deposition parameters: a substrate temperature of T_g =260 K and a deposition rate of $(4.2\pm0.3)\times10^{-3}$ ML/s. Figure 2(a) shows the evolution of the specular intensity during deposition of Ag onto the bare substrate. The intensity decreases monotonically, indicating the development of 3D structures because of hindered interlayer mass transport. (b)-(e) show the evolution of the specular intensity during deposition of Ag onto substrates which have been prepared with a high density of nuclei by depositing 0.05 ML of Ag at the indicated preparation temperatures T_p and a deposition rate of 4.3×10^{-2} ML/s. As stated above, after heating to 260 K, the starting situation for the growth experiment is a substrate with small islands of compact shape but different density, the density increasing with decreasing preparation temperature, i.e., from (b)-(e) in Fig. 2. With increasing island density, a transition is observed from the monotonic decay of the signal to a behavior characteristic for 2D growth: The intensity runs through a minimum and has a maximum after deposition of the amount of Ag corresponding to one monolayer. The intensity in the max-

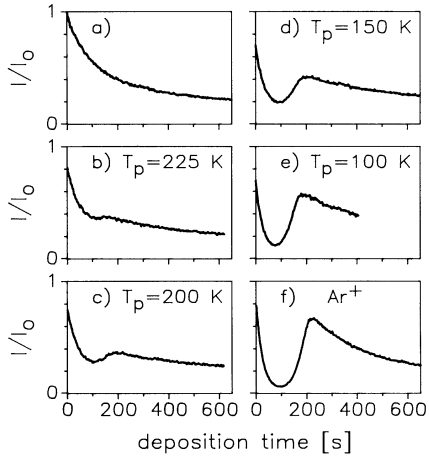

FIG. 2. Evolution of the He specular peak height during deposition of Ag at a rate of $(4.2\pm0.3)\times10^{-3}$ ML/s and a substrate temperature of 260 K onto substrates prepared in a different way: (a) bare substrate, (b)-(e) substrate prepared with a high density of nuclei by predepositing 0.05 ML of Ag at the indicated preparation temperature T_p and a rate of 4.3×10^{-2} ML/s, (f) substrate sputtered by bombardment with 600 eV Ar^+ ions at a substrate temperature of 260 K for a short time corresponding to the removal of 0.014 ML of Ag.

imum increases with increasing island density indicating an improved quality of the 2D layer (i.e., less material in the second layer after deposition of 1 ML), and, therefore, increasing interlayer mass transport. For coverages beyond one monolayer, no oscillations are observed. This is the expected behavior, because an enhanced density of nuclei is only prepared in the first layer. If this first layer is nearly completed when nucleation in the second layer starts, the density of nuclei in the second layer equals that on the bare substrate resulting in multilayer growth.

The second method to prepare the substrate with an enhanced density of Ag nuclei is to sputter the surface prior to deposition by low energy Ar^+ ion bombardment at the growth temperature. During the ion bombardment, not only atoms are removed from the surface, but also adatoms are created *on top* of the substrate layer, as has been demonstrated for the case of Pt(111) by STM [13]. These adatoms nucleate to form adatom islands with a density higher than that formed during growth on the bare substrate at the same temperature [14]. This may be attributed to a reduction of the diffusivity of the generated adatoms in the presence of vacancies (or vacancy clusters). Alternatively, adatoms generated in a correlated way upon the impact of a single ion could form small clusters in the vicinity of the impact position. Figure 2(f) shows the evolution of the specular peak height during deposition of Ag onto Ag(111) after having removed 0.014 ML of Ag by 600 eV Ar^+ sputtering. Again, 2D growth of one monolayer is observed.

These experiments establish the central result of the present Letter: Interlayer mass transport can be enhanced by deliberately increasing the island density. Even for a system like Ag/Ag(111) which grows in a multilayer mode in the whole temperature range studied to date, this effect can be utilized to achieve 2D growth (of at least one layer). A straightforward explanation for the enhanced interlayer mass transport can be given as follows: In order to descend from an island, atoms deposited on top have to reach the island edge and overcome the barrier for diffusion over the island edge. If the barrier is active, atoms will have to try several times before succeeding in descending from the island. By reducing the island dimensions without reducing the mobility of adatoms on top, the visiting frequency of the edge and therefore the attempt frequency of adatoms to descend the island edge is increased, resulting in an enhanced interlayer diffusion. It has also been proposed that the barrier height itself depends on the island dimensions, decreasing or even vanishing for small islands [7], which would, of course, also lead to an increased interlayer mass transport. A clear distinction between the two effects cannot be made in a straightforward manner and would certainly involve model assumptions. We will address this issue in a full paper. We can, however, relate our results to the surfactant-induced layer-by-layer growth and develop a model for the role of Sb *without* a *direct* influence on the activation barrier. The presence of 0.2 ML of Sb on the Ag(111) substrate reduces the mobility of Ag adatoms and the result is a high island density. It has been assumed that the Sb remains on the substrate layer until the islands coalesce and the Sb is pushed onto the first grown layer [8]. According to this picture, no Sb is present on top of islands before their coalescence and the mobility of adatoms on top of islands is not reduced leading to a high attempt frequency for descent. This is exactly the situation we have mimicked in our experiments on the clean system and, therefore, we conclude that the interlayer mass transport in the presence of Sb is already enhanced without any further direct influence of Sb on the barrier height. It might even be that the surfactant counteracts the dominating effect of the high island density by hindering the descent from island edges. Therefore, the direct reduction of the barrier height by the surfactant as proposed in [8] cannot be simply followed from the observation of layer-by-layer growth as long as an enhanced island density is also observed.

In view of further applications of our results we extended the possibility of growth mode manipulation on several layers. So far, we have only presented experiments in which *one* two-dimensional layer was grown. Further growth proceeded in a multilayer mode because an enhanced island density was only prepared in the first layer. The advantage of a surfactant like Sb is that it is not incorporated in the growing crystal but is pushed up into the outermost growing layer. Thus, it has the same influence on any consecutive layer and a layer-by-layer growth results. The same can be achieved without surfactants by using a pulsed ion beam during deposition of Ag onto the crystal. The ion beam is turned on for a short period just when growth in a particular layer starts in order to produce an enhanced island density in that layer. The result of such an experiment is shown in Fig. 3. While Ag was continuously deposited at a rate of 0.005 ML/s onto the substrate held at 300 K, a short pulse of 600 eV Ar^+ ions was directed onto the surface at

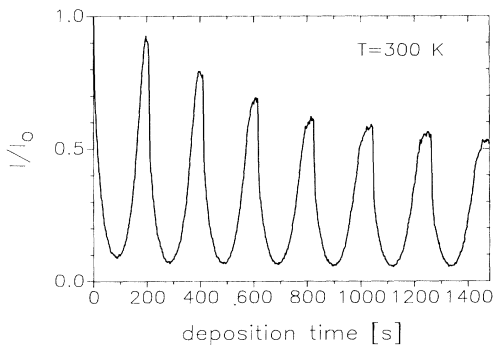

FIG. 3. Evolution of the specular peak height during deposition of Ag at a rate of 4.7×10^{-3} ML/s and a substrate temperature of 300 K. At the start and in the maxima a short sputter pulse (600 eV, Ar^+) corresponding to the removal of 0.014 ML of Ag was given.

the beginning and then after deposition of each monolayer (i.e., in the maxima of the intensity). The pulse length was 1 s, corresponding to the removal of 0.014 ML of Ag. As judged from the persistent oscillations, several layers can be grown in a layer-by-layer mode, qualifying this method for a possible application in thin layer fabrication.

It is important to note that we never succeeded to produce layer-by-layer growth, if both deposition *and* sputtering were done continuously. This observation supports the picture developed above: Interlayer mass transport is enhanced if the mobility of adatoms *in* the growing layer is limited (so that a high island density is formed), but not *on top* of the growing islands before they coalesce and the layer is completed. By continuously sputtering, this requirement is not fulfilled: Because of the ion impact, small islands are formed on any exposed area and therefore also on top of growing islands. Consequently, the adatom mobility is hindered both in the growing layer and on top, and the interlayer mass transport is hardly enhanced. This idea can again be linked to our model description of the surfactant-mediated growth assuming no direct influence on the activation barrier: If Sb is present to the same extent both in the growing layer and on top, the interlayer mass transport should not be enhanced. As the Sb precoverage in the experiments by van der Vegt *et al.* [8] was as low as 0.2 ML, it could be assumed that the Sb remains in the growing layer until it is almost completed and growing islands are not covered by Sb. We speculate that for higher coverages of Sb, the interlayer mass transport should be less efficient and layer-by-layer growth should not be observed.

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