Surfactant-Induced Layer-By-Layer Growth of Ag on Ag(111)

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We have investigated the epitaxial growth of Ag(111) by x-ray reflectivity experiments. In the temperature range from 175 to 575 K the growth mode changes gradually from three-dimensional to step flow, but at no temperature was layer-by-layer growth observed. Submonolayer deposits of Sb on the starting surface dramatically alter the growth behavior. With Sb the Ag grows layer by layer over the entire temperature range investigated (225–375 K), resulting in smoother surfaces at the lowest growth temperatures. We propose that Sb decreases the barrier for interlayer diffusion.

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A detailed understanding of the mechanisms involved in the epitaxial growth of metals is not only of fundamental interest, but also has technological importance. For the growth of magnetic films or multilayer structures for x-ray mirrors, a good control of the interface structure and surface flatness is important in order to obtain the best layer properties [1,2].

Recent studies have shown that it is possible to grow relatively flat metal layers at very low temperatures. Egelhoff and Jacob [3] used reflection high-energy electron diffraction (RHEED) oscillations to show that some metals grow layer by layer at temperatures as low as 77 K. Using thermal energy atom scattering, Kunkel *et al.* [4] recently discovered a very interesting behavior for the growth of Pt on Pt(111): As a function of decreasing temperature, the system showed first layer-by-layer growth, then three-dimensional (3D) growth, and after that again layer-by-layer growth. This "reentrant" layer-by-layer growth was explained in terms of an island-size-dependent barrier for interlayer diffusion; atoms can more easily jump off small islands than off larger ones.

In this Letter we show that smoother layers can also be grown by using a surfactant. Surfactants have been used in the past to influence heteroepitaxial growth of semiconductors [5,6]. Steigerwald, Jacob, and Egelhoff [7] did investigate the influence of adsorbed gases on metal growth. Here we have for the first time successfully applied a surfactant in the homoepitaxial growth of a metal crystal. We have investigated the growth of Ag on Ag(111) using the technique of x-ray diffraction. Because kinematical theory applies, this technique yields detailed information on the growth mode and surface morphology, which can be obtained *during* crystal growth [8].

The experiments were performed at the surface x-ray diffraction station 9.4 of the wiggler beam line at the Synchrotron Radiation Source in Daresbury (United Kingdom), using focused radiation with a wavelength of 0.9 Å. The setup consists of an ultrahigh vacuum chamber coupled to a five-circle diffractometer [9]. In order to remove the surface damage from the polishing treatment, the Ag(111) sample (diameter 10 mm, miscut $<0.05°$) was annealed for 3.5 h at 975 K. Because of the high vapor pressure of Ag this treatment removed ~ 2 μm of material and reduced the surface mosaicity from 2° to 0.1° full width at half maximum. After that the sample was cleaned by repeated cycles of annealing (20 min, 875 K) and sputtering (45 min, 575 K, 800 eV Ar^+, 0.5 $\mu\mathrm{A/cm}^2$). Two Knudsen effusion cells were used for Ag and Sb deposition. For Ag the deposition rate was ~ 0.02 monolayer (ML) per second, for Sb ~ 0.002 ML/s.

In the first part of the experiment, we grew Ag on Ag(111) without using a surfactant. The intensity of the specularly reflected beam was measured during Ag deposition. The acceptance of the detector was 0.02 $\mathrm{Å}^{-1}$ in the in-plane direction and 0.08 $\mathrm{Å}^{-1}$ along the surface normal. The incident angle was 5.5°, corresponding to destructive interference between reflection from two consecutive (111) planes. In reciprocal-space coordinates this is the $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ "anti-Bragg" reflection where maximum sensitivity for surface roughness and growth mode is obtained [8]: In the case of step-flow growth arriving adatoms are incorporated at existing step edges resulting in a constant reflected intensity. When the atoms nucleate on a flat terrace and form two-dimensional (monolayer height) islands, the growth proceeds in a layer-by-layer fashion. This yields intensity oscillations due to the destructive interference between islands and terrace. The damping of these intensity oscillations is a measure of the quality of the layer-by-layer growth. When no interlayer diffusion occurs, three-dimensional islands are created and this 3D growth causes a decaying reflectivity.

The results are shown in Fig. 1 for a number of substrate temperatures. No intensity oscillations are observed, indicating that growth does not proceed in a layer-by-layer mode at these temperatures. At 575 K the reflected intensity is constant which indicates step-flow growth. For lower temperatures the signal decreases monotonically. For temperatures of 375 K and above, a

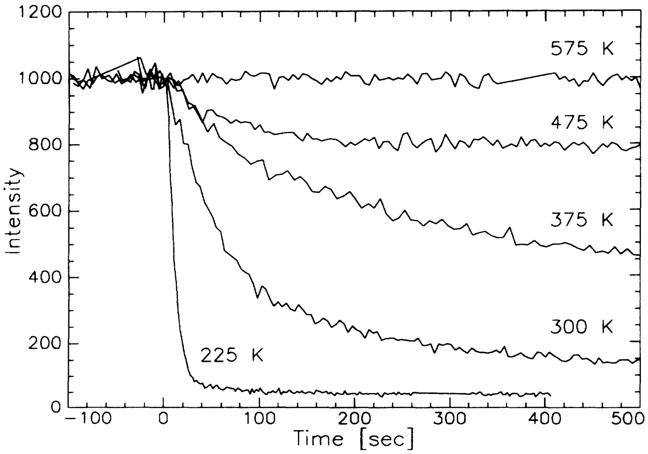

FIG. 1. The intensity of the $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ reflection during Ag deposition. Shown are a set of curves corresponding to different substrate temperatures. The curves are normalized to a starting signal of 1000.

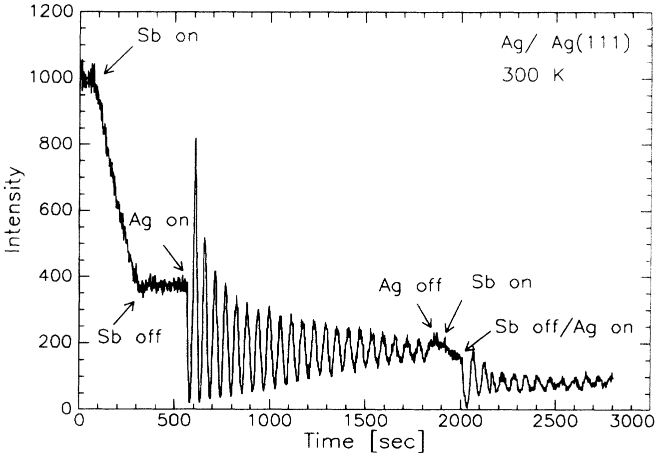

FIG. 2. The intensity of the $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ reflection during successive deposition of Sb (0.2 ML) and Ag at 300 K. At $t=0$ the Ag deposition started. The intensity is normalized to a starting signal of 1000.

partial recovery of the reflected signal was observed after stopping the deposition. A complete recovery occurred only after annealing to 875 K. At 225 K the intensity drop closely follows the exponential behavior expected for Poisson statistics, i.e., growth without interlayer diffusion. There is a large difference in the literature between the experimental and calculated diffusion length (~15 Å and ~1 mm, respectively, at 225 K and our deposition rate) [10]. A diffusion length of 1 mm would result in step-flow growth for the entire temperature range investigated and therefore in our experiment the diffusion length must be much smaller. It is unlikely that contamination causes the observed behavior, because the growth at 575 K shows no intensity decrease at all and no changes occurred after additional cleaning cycles. Also the substrate is very flat as shown by the initial reflected signal and by measuring the intensity along a number of crystal truncation rods; the latter indicate a rms roughness of ~1 Å [11]. The observed behavior is consistent with RHEED measurements [12] and with recent molecular dynamics simulations [13]. Data at 175 K (not shown in Fig. 1) are virtually the same as at 225 K; no evidence for reentrant layer-by-layer growth was found at this temperature.

Next we investigated the influence of Sb on the growth behavior. The result for a substrate temperature of 300 K is shown in Fig. 2. The initial decrease in intensity is caused by the deposition of 0.2-ML Sb. This small amount of Sb completely alters the growth behavior of the subsequently deposited Ag. Now strong oscillations are observed indicating layer-by-layer growth over more than 20 ML. A small additional amount of Sb halfway through the deposition (see Fig. 2) leads to an enhancement in the oscillation amplitude. Apparently the amount of Sb on the surface has decreased during the growth. The constant reflected signal after the initial Sb deposition shows that no thermal desorption occurs. Thus either Sb is lost by Ag-deposition-stimulated desorption (possibly during an exchange mechanism) or Sb is incorporated. The Sb incorporation must be very low because the oscillations are very persistent. Low incorporation is consistent with the observations of As segregation during metal deposition on GaAs [14].

In order to get a better understanding of the influence of Sb, we grew Ag at two more substrate temperatures. The results are shown in Figs. 3(a) and 3(b). For comparison the data obtained without Sb are plotted as well. We see at both temperatures the occurrence of layer-by-

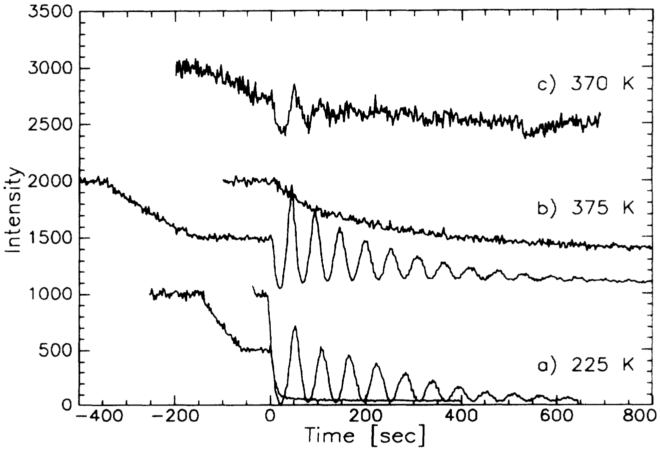

FIG. 3. The intensity of the $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ reflection after a fraction of a ML Sb was added at different substrate temperatures. (a) 225 K, 0.14 ML Sb; (b) 375 K, 0.15 ML Sb. For comparison the intensities without addition of Sb are plotted as well. In (c) the $(\frac{1}{2}\,\frac{5}{2}\,\frac{\bar{3}}{2})$ reflection is shown: 370 K, 0.06 ML Sb. The intensity is normalized to a starting signal of 1000; (b) and (c) have vertical offsets of 1000 and 2000, respectively.

layer growth.

The specularly reflected beam has only momentum transfer along the surface normal and therefore probes only the height distribution of the deposited atoms. In order to investigate the in-plane crystalline quality of the growing film we performed one deposition while measuring the $(\frac{1}{2}\,\frac{5}{2}\,\overline{\frac{3}{2}})$ reflection, which also has an in-plane momentum transfer component [see Fig. 3(c)]. The reflected signal is much weaker, but the data nevertheless clearly show the initial decrease due to the Sb deposition and the oscillations during Ag growth, indicating that both species are located on lattice sites.

The x-ray data do not give direct information about a possible microscopic mechanism responsible for the observed behavior, but we suggest that the Sb has a large effect on the interlayer diffusion barrier. The fact that no layer-by-layer growth occurs for Ag(111) without Sb may be explained by assuming that the interlayer diffusion barrier is so high that it is not possible for newly arriving atoms to jump off an island at the temperatures investigated. Such barriers for interlayer diffusion have been observed in field-ion microscopy studies on W(110) [15] and Ir(110) [16] surfaces and were postulated by Kunkel *et al.* [4] to explain their observed reentrant layer-by-layer growth.

An attractive model for the role of Sb in the growth of Ag(111) is that it lowers the barrier for interlayer diffusion by attaching itself to island edges. This occurs for many impurities on clean surfaces. Then Ag atoms can move to the next lower level and growth proceeds more in a layer-by-layer fashion. This also explains why only submonolayer fractions of Sb are necessary. During growth the Sb is pushed forward as the islands grow until the islands coalesce and the Sb presumably moves one level up. This is a good description of the observations with and without Sb at 225 K shown in Fig. 3(a). The data in Fig. 3(b) indicate that Sb also has an additional effect. For the case with Sb the first minimum in the reflected signal is reached very quickly, when the signal without Sb is still fairly strong. This shows that Sb acts as a nucleation center for island growth leading to many small islands and therefore to the minima in the reflected intensity. This effect is only observable at the high substrate temperatures since at low temperatures the Ag itself already forms nucleation centers.

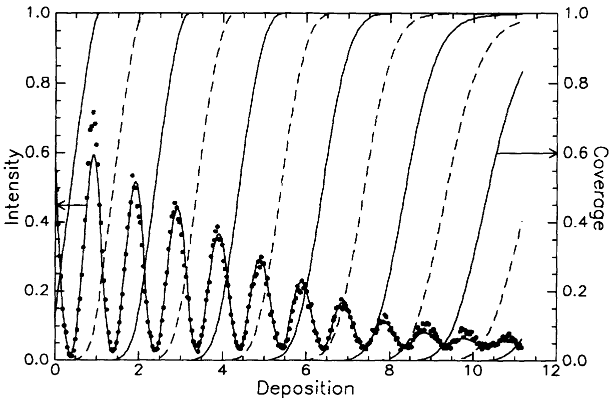

FIG. 4. Normalized reflection intensity during Ag deposition on Ag(111) with Sb at 225 K (dots) together with a fit (solid curve) obtained using the rate equations model ($\alpha=3.6$, $\beta=0.85$; see text). The coverage per layer is plotted as well. Odd and even layers are represented by solid and dashed curves, respectively.

The addition of Sb leads to smoother surfaces at 300 and 225 K. In order to have a quantitative estimate of the roughness during growth we have used a simple rate equations model to fit the data with Sb at 225 K. In this model, which is similar to the one of Cohen *et al.* [17], the surface layer n has a coverage θ_n. When the deposition rate is R, then $R(\theta_n-\theta_{n+1})$ atoms are deposited per unit time at level $n+1$ (on top of level n) and a fraction λ_n of this amount diffuses to level n. This yields the following set of coupled differential equations:

$$\frac{d\theta_n}{dt}=(1-\lambda_{n-1})R(\theta_{n-1}-\theta_n)+\lambda_n R(\theta_n-\theta_{n+1})\,, \qquad (1)$$

with

$$\lambda_n=1-\exp\left[\frac{-\alpha\beta^n\left(\frac{1}{2}-\left|\theta_{n-1}-\frac{1}{2}\right|\right)^{1/2}}{\theta_{n-1}}\right], \qquad (2)$$

where α and β are parameters characterizing the amount of interlayer diffusion and where the functional form of λ_n is chosen on semiempirical grounds [18]. $\alpha=\infty$ results in perfect layer-by-layer growth and $\alpha=0$ in Poisson growth. The difference with Cohen's model [17], which did not yield a good fit, is that the interlayer diffusion is made level dependent through the parameter β. This is reasonable because during growth the amount of Sb will decrease and the island size may change [4]. Solving Eqs. (1) and (2) yields the coverage per layer versus time. The reflected intensity can be directly calculated from the coverage using the kinematic approach valid for x rays [8]. In Fig. 4 the results of fitting the parameters α, β, and R to the observed intensities are shown. Even though Eqs. (1) and (2) are a simplified description of the growth process, the good agreement with the experimental intensities shows that the equations do yield a reasonable estimate of the coverage per layer. As Fig. 4 shows, the number of simultaneously growing layers does not exceed four during deposition at 225 K.

When comparing the growth oscillations at different temperatures we see a varying behavior of the intensities at the minima. At present it is hard to give a definitive explanation for this but it is likely to be caused by a changing island-size distribution due to a decreasing Sb concentration during growth. This leads to a varying width of the diffuse intensity which causes a changing fraction of this diffuse intensity to be accepted by the detector. For islands with a coherence length of ~150 Å about 10% of the diffuse intensity is collected by the detector [19]. We did not perform peak profile scans, which can verify this interpretation.

In summary, we reported the use of Sb as surfactant in order to change the 3D growth mode of Ag(111) into the layer-by-layer mode, resulting in much smoother surfaces at the lowest growth temperatures. In order to explain our observations, the Sb is suggested to lower the interlayer diffusion barrier and to act as a nucleation center for island growth. More experiments, also on a microscopic scale, need to be done in order to get a full understanding of our observations.

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