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The multilayer growth mode in the epitaxy of Ag on Ag(111) analysed by SPALEED

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Abstract

The morphology of atomically stepped hillocks formed during homoepitaxial growth on Ag(111) is analysed by SPALEED in the deposition range of 0–20 monolayers (ML). At 220 K the inclination of the facets increases linearly with coverage, with the terrace widths being correspondingly reduced. Facets with (100)-like steps are preferred over those containing (111)-like steps resulting in a more triangular shape of the hillocks. At room temperature the hexagonally shaped hillocks are larger owing to enhanced terrace widths. Moreover, the beginning interlayer diffusion limits the height of the hillocks to ~ 10 layers effecting a much slower reduction of the terrace widths after deposition of 3.7 ML.

1. Introduction

The investigation of the growth mode in the metal-on-metal epitaxy is an object of current interest as the physical properties of thin films most strongly depend on their particular structure. It was demonstrated that for a given material the growth mode – and thus the film morphology – can be varied most sensibly from multilayer (3D) to layer-by-layer (2D) growth if the substrate temperature and the deposition rate are changed [1]. Most recently, some surprising results have been obtained, viz. as to Pt on Pt(111) the reentrant layer-by-layer growth at temperatures below those where 3D growth occurs [2], or the surfactant-mediated layer-by-layer growth for Ag on Ag(111) realized by a predeposition of 0.2 monolayer (ML) of Sb on the substrate [3]. These facts have drawn the attention to the size of the growing nuclei. It seems that for a given deposition the interlayer mass transport as a prerequisite to 2D growth is the more probable the smaller the nuclei are (or the higher the density of nuclei is) which recently was impressively demonstrated for the very Ag/Ag(111) system [4].

On the other hand, up to now only little attention has been paid to the quantitative analysis of the surface morphology of the growing film. The only detailed study known to the authors is published by Meyer et al. [5] for an ultrathin epitaxial copper film of a fixed thickness of 2.5 ML under various deposition conditions. Using the spot profile analysis of low-energy electron diffraction (SPALEED) Meyer et al. obtained a lot of information on the film morphology.

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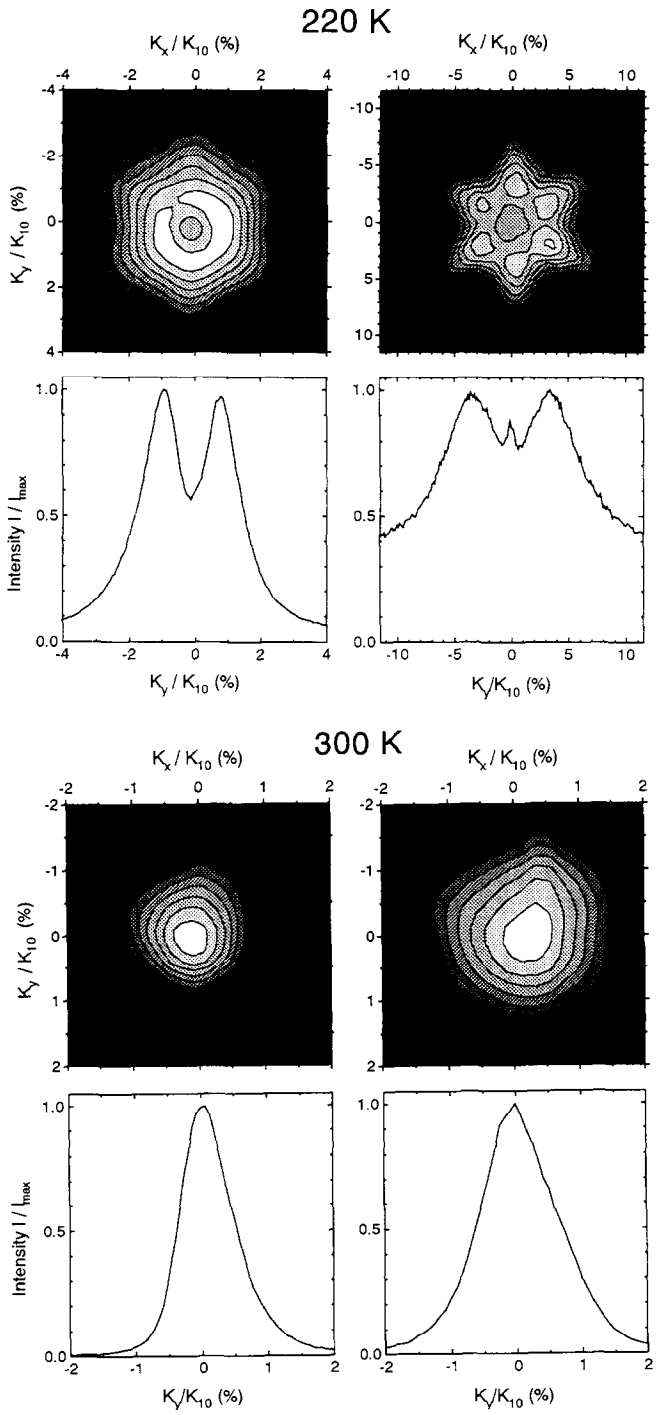

Fig. 1. Two-dimensional intensity distributions (above) and one-dimensional spot profiles (below) under out-of-phase condition after deposition of 2 ML (left) and 16 ML (right) Ag on Ag(111). The scattering vectors K_x and K_y are normalized to the next spot distance K_{10}. Note the different scales for clarity. The grey scale plots are drawn to a logarithmic scale, contour lines indicate constant intensities.

The present paper is concerned with the morphology of Ag layers epitaxially grown without surfactants on Ag(111) for a relatively wide deposition range up to 20 ML. Meinel et al. [6] and van der Vegt et al. [3] have shown that the silver homoepitaxy on Ag(111) is characterized by a multilayer growth mode. At 225 K the growth occurs without interlayer diffusion, i.e. it obeys the Poisson statistics. At higher temperatures the mobility of the atoms increases entailing a flattening of the growth hillocks by larger terrace widths by enhanced intralayer diffusion and beginning interlayer diffusion. Van der Vegt et al., however, have not observed any indication of two-dimensional islands forming, before at 575 K pure step flow occurs. The present study only deals with the low temperature range of 220–300 K, where the influence of the beginning interlayer diffusion can be studied.

2. Experimental

The experiments were performed in a home-made high-resolution SPALEED instrument following the development of the Henzler group [7]. The transfer width of the instrument was determined to be ~ 2000 Å. The silver substrate was produced by fast solidification of a droplet on a graphite mould in high vacuum to a monocrystalline silver sphere of 5 mm in diameter. Atomically flat Ag(111) growth faces were obtained by electrolytic growth [6]. After the Ag(111) surface is optically oriented by laser illumination half the sphere was removed by chemical cloth polishing in order to obtain the largest surface plane. Carrying out several cycles of ion sputtering and annealing in ultra-high vacuum the substrate surface was checked by SPALEED revealing that the surface is composed of mosaics having a mean misorientation of 0.02°. The mean step distance in the mosaics is ~ 1000 Å, which transmission electron microscope (TEM) studies had proved before for electrolytically grown Ag(111) surfaces, too [8].

Silver films were evaporated with a deposition rate of 0.5 and 2 ML/min, controlled by a quartz oscillator. The deposition was interrupted for measuring one- and two-dimensional intensity distributions of the specular spot, before the evaporation continued. Recovery effects were not detected, which is compatible with results of van der Vegt et al. [3].

3. Results and discussion

Fig. 1 compares spot shapes and profiles measured under out-of-phase condition of epitaxial silver films of a mean thickness of 2 and 16 ML, deposited on Ag(111) at 220 and 300 K. Two features are obvious. At 220 K the spot shape has a hexagonal structure weakly beginning at already 1 ML and modified to a more asterisk-like structure at high coverage. At 300 K, however, a hexagonal spot shape seems to develop only at higher coverages. The earlier TEM studies revealed hexagonally shaped growth hillocks at 300 K [6], their lateral dimensions, however, are too large to be satisfactorily resolved by SPALEED. The second feature is spot splitting (satellite spots) at 220 K indicating the existence of facets whereas at 300 K there only is a spot profile broadening at higher film thicknesses. To characterize the film morphology, on the one hand the evolution of spot splitting at 220 K is analysed, and on the other hand that of spot broadening at 300 K under varying coverage is studied.

Spot splitting was detected already at 1.5 ML. The energy dependence of the splitting distance for a fixed coverage of 16 ML was tested revealing that the satellites are arranged on reciprocal lattice rods which are inclined to those of the (111) surface. The inclined lattice rods can be connected with facets on the surface formed by the layers deposited. Thus, the separation ΔK_s of the satellite spots normalized to the next spot distance can be transformed in a facet angle α. Under out-of-phase conditions $S = (2n + 1)/2$ with n = integer and $S = K_z d/2\pi$ given by the perpendicular component of the scattering vector and the interlayer distance, one obtains $\tan \alpha = \sqrt{8/9}\,\Delta K_s$. Fig. 2 shows that the facet angle increases linearly described by the simple relation $\alpha_{220\,\mathrm{K}}(^\circ) = 0.5 + 0.2\theta$ with θ being the coverage. The existence of satellite spots implies that the

distribution of terrace widths forming the facets cannot be very wide. A fit, which compares the slit intensities (integrated perpendicularly to the analysing spot profile) with theoretical data calculated from one-dimensional surface morphologies using layer-dependent terrace width distributions [9], indeed yields gamma distributions with strongly reduced probabilities of short terrace widths. Assuming monatomic steps between the terraces the mean terrace width perpendicular to the steps can easily be derived by $\langle W_{220\,K}\rangle = \sqrt{3/8}\ a_0/\Delta K_s$ with a_0 being the lattice constant. Accordingly, the mean terrace width in the deposited film reduces from 165 ± 13 to 37 ± 5 Å for a mean film thickness increasing from 1.5 to 16 ML.

A similar analysis is given in Fig. 3 for Ag deposition on Ag(111) at room temperature. Initially, there is a strong increase of the spot broadening indicated by the full width at half maximum (FWHM) of the spot profiles normalized to the Brillouin zone followed by a very slow increase at higher deposition. The linear regression fit yields $\mathrm{FWHM}_1 = 0.60 + 0.169\theta$ for $\theta < 3.72$ ML and $\mathrm{FWHM}_2 = 1.17 + 0.016\theta$ for $\theta > 3.72$ ML. The mean terrace width perpendicular to the steps can easily be estimated from these values by

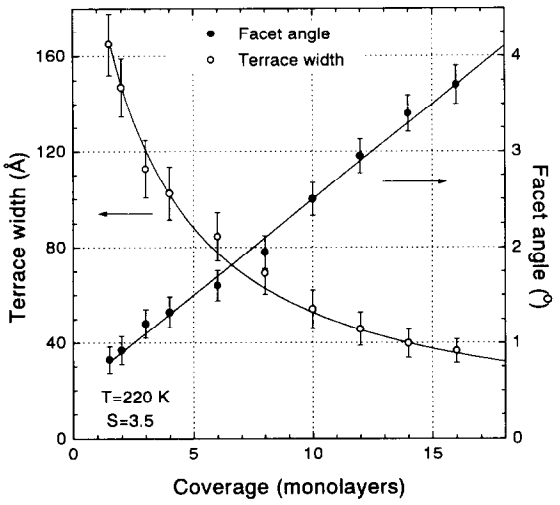

Fig. 2. Facet angles and mean terrace widths of atomically stepped growth hillocks after Ag deposition on Ag(111) at 220 K derived from spot splitting under out-of-phase condition.

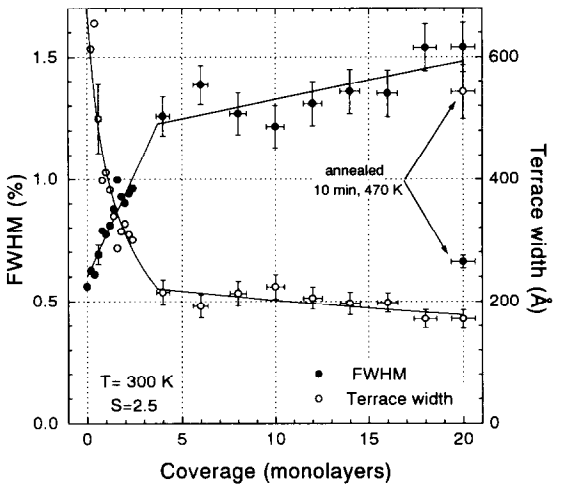

Fig. 3. Full width at half maximum (FWHM) of spot profiles normalized to the Brillouin zone under out-of-phase condition and derived mean terrace widths of atomically stepped growth hillocks after Ag deposition on Ag(111) at 300 K.

$\langle W_{300\,K}\rangle = \sqrt{3/8}\,a_0/\sqrt{\mathrm{FWHM}^2 - T_w^2}$ assuming a simple Gaussian deconvolution with the instrument function T_w. The initially strong decrease of the terrace widths can be explained by the increase of the step density as a consequence of repeated 2D nucleation on top of the islands already formed, realising the multilayer growth mode. Thus, the slow reduction of the terrace widths for depositions > 3.7 ML is thought to be caused by a nearly *fixed* number of incomplete atomic layers, i.e. further growth is mainly attributed to atoms being captured at steps (step flow), whereas the 2D nucleation on the highest atomic layer is largely compensated by a fill-up of the lowest incomplete layer. Both processes can be influenced by a small percentage of *interlayer* diffusion. After the Poisson statistics the original surface is covered by 97.6% and nine layers have a coverage > 1% if 3.7 ML are deposited on it. We conclude that the growth at room temperature is characterized by the formation of atomically stepped hillocks initially growing up to 10 layers in height. This morphology is then essentially maintained after further deposition. On the other hand, it should be pointed out that the discussion about coverages in the individual layers is very indirect. Only distances up to 2000 Å

can be reliably resolved by SPALEED. This is roughly the basic area of one growth hillock with 5 layers and terrace widths of 200 Å. That means, at high coverages we detect only sections of the hillocks by interference effects, the statistics is essentially given by the *incoherent* superposition of a great number of such different sections composed of a different number of atomic layers. The determination of the mean terrace widths is, however, not affected as the surface is projected on a two-level surface under out-of-phase conditions.

The question remains open why we do not observe spot splitting at 300 K. Hillocks with terrace widths of 200 Å form facets inclined by 0.68° to the surface and the separation of the satellite spots is 1.25% detectable by our SPALEED instrument only if the terrace widths are distributed rather closely about the mean value. Model calculations using nth-order gamma distributions for the terrace widths reveal that splitting can be detected for $\langle W \rangle = 165$ Å and $n = 4$, but no longer for $\langle W \rangle = 200$ Å, as the latter requires at least $n = 8$–10. A detailed one-dimensional analysis of the measured spot profiles yielded the result of $n = 2$–4 for a deposition of 1 ML. Now the facet angle can be determined since the terrace widths are known. At the initial stage of epitaxy < 3.7 ML it increases up to 0.62°, afterwards it rises only slowly to 0.76° after the deposition of 20 ML.

A strong interlayer mass transport takes place if the deposited film is annealed at higher temperatures. Annealing a film of 20 ML in thickness at 470 K for 10 min effects a triplication of the mean terrace width explainable only by a smoothing of the film surface leaving only few incomplete surface layers comparable with a deposition below 1 ML at 300 K.

In Fig. 4, two-dimensional intensity distributions are compared for three different phases. The *sixfold* symmetry under out-of-phase condition ($S = 3.5$) is reduced to a *threefold* symmetry if the phase is varied with the position of the three satellite spots being alternatively below and above $S = 3.5$. Even if this result is not very distinct it clearly indicates the more triangular shape of the growth hillocks deposited at 220 K, also revealed for Pt on Pt(111) at low coverages by scanning tunneling microscopy [10] and for Cu on Cu(111) [11]. A crystallographic analysis shows that the steps of the (100)-type are preferred over those of the alternative (111)-type. More exact statements require, however, the calculation of two-dimensional intensity distributions for such growth models. The growth mechanisms and the inherent diffusions processes possible will be discussed later on.

4. Conclusion

SPALEED is a powerful method of quantitatively characterizing the multilayer growth mode in the metal-on-metal epitaxy demonstrated by

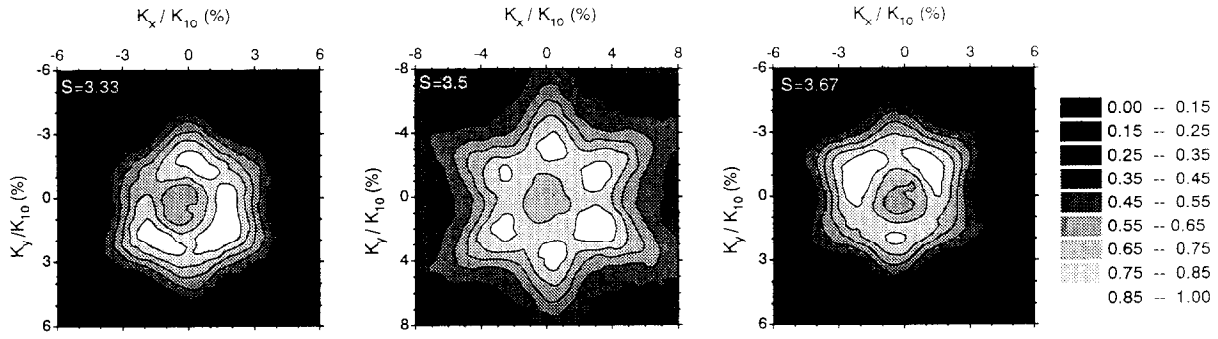

Fig. 4. Two-dimensional intensity distributions for different phases after deposition of 16 ML Ag on Ag(111) at 220 K. The three satellite spots are alternatively arranged below and above the hexagonal arrangement under out-of-phase condition. Note the different scales for clarity.

the determination of the morphology of atomically stepped hillocks formed during the epitaxy of Ag on Ag(111). At 220 K spot splitting is observed with the facet angle of the hillocks linearly increasing with the deposition, correspondingly decreasing the terrace widths. After the Poisson statistics the number of incomplete layers increases by repeated 2D nucleation. At 300 K hillocks of finite height are formed at the initial stage of deposition. The further growth is mainly determined by step flow, whereas the nucleation on the highest atomic layer is largely compensated by a fill-up of the lowest incomplete layer. A large smoothing of the film morphology can be reached by annealing at higher temperatures. Two-dimensional intensity distributions indicate that at 220 K the islands have a more triangular shape with dominant (100)-like edges.

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6. References

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