The STM view of the initial stages of polycrystalline Ag film formation

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\textbf{Abstract.} The growth of Ag thin films deposited at 300 K on amorphised Si surfaces under ultra high vacuum conditions is investigated by \textit{in situ} scanning tunnelling microscopy. The analysis of film morphology as a function of film thickness together with additional annealing experiments allow a quite complete picture of the film formation processes to be obtained.

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1. Introduction

Polycrystalline thin metal films are one of the most important and best studied class of thin film systems. They have wide applications; among them are their use as interconnects in integrated circuits, magnetic storage media, catalytic elements, thermal sensing elements, and as protective and decorative coatings [1]. Due to the intimate link of film properties with film structure, their performance and reliability are determined to a large extent by their adhesion, texture, grain distribution and overall morphology.

Based on their conceptual and chemical simplicity, in past decades thin metal films have acted as the fruit fly of the science of thin solid films. The question of thin metal film structure and morphological evolution and their dependence on deposition parameters was, with steadily improving analytical tools, at the centre of scientific interest. This research leads to the development of structure zone models, which collect the fundamental knowledge of thin film structure on deposition parameters and impurities [2]–[7].

Although the rough lines are clear by now, not enough and actually not much is known about the atomistic details during the decisive early stages of thin metal film growth. To give an example, in recent years the stress evolution during polycrystalline thin metal film growth of relatively low melting metals like Ag and Cu was thoroughly investigated [8]–[14]. However the link between stress state and film morphology is far from understood. This statement is particularly true for a reversible compressive stress component during film growth. Upon growth interruption, a significant change in the stress state towards tensile stress occurs on the timescale of seconds or minutes. If growth is continued, the compressive stress component re-establishes. Although it is evident that the stress change must be linked to deposition induced morphological changes, there is no agreement about what these changes are.

In the past, transmission electron microscopy (TEM) during thin metal film growth has been an extremely instructive and powerful tool for the investigation of thin film growth processes, e.g. to uncover the decisive influence of impurities on the growth [15]–[18]. A new and in some respects more powerful tool is scanning tunnelling microscopy (STM). It can give detailed information on the morphology and processes at the growth front like film roughness, facet formation, step distributions and so forth which are largely inaccessible to other microscopic methods. Although STM is a well established method by now, there has been very little STM work on polycrystalline films published. There is a remarkable piece of work on the annealing behaviour of a polycrystalline Au film [19], but, to the authors best knowledge, nothing has been published on the early stages of polycrystalline film formation. Possible reasons for this situation may be the difficulty of imaging the rough complex structured surfaces of such films without tip artifacts and without severe tip–surface interactions or the necessity of an ultra high vacuum (UHV) surface science approach to film formation and analysis.

Here we study the initial stages of Ag thin film formation on an amorphous substrate by STM under extremely clean conditions. The STM investigations are complemented by x-ray diffraction (XRD) and TEM measurements. The growth of Ag on an amorphous substrate can be considered as a prototype system for film formation. Amorphized Si was used as a substrate due to our ability to prepare this substrate in a completely reproducible way through ion bombardment induced amorphization under UHV conditions. Ag forms no silicide with Si and does not intermix with it [20]. As the amorphous substrate is stable up to 750 K, it allows temperature dependent growth studies. In this paper we report mainly on growth at 300 K supplemented by a few low temperature growth and annealing experiments.
Ag thin film growth on amorphous substrates has been studied in the past by diffraction and microscopic methods. As a last part of this introduction, we review some of the known facts. Diffraction measurements [21]–[23] agree that for clean deposition conditions and relatively low rate at room temperature and somewhat above, after an initial random orientation a (111) out-of-plane texture (also called fibre texture or one degree ordered texture) develops at a film thickness of the order of 50 nm, i.e. the (111) planes of the crystallites tend to be parallel to the substrate surface. Thickness dependent TEM measurements of the Ag film morphological evolution on a polycrystalline MgF₂ layer showed the following growth stages [24]: (i) nucleation of a high density of islands (Volmer–Weber growth mode); (ii) incomplete island coalescence at a thickness of 2–3 nm leading to first grain boundaries (GBs); (iii) percolation of the film at about 11 nm while narrow trenches (channels) remain, which separate elongated, polycrystalline island structures; (iv) film closure at about 22 nm; (v) further thickness increase is accompanied by considerable grain growth. Although differing in the relevant thicknesses, this picture is very similar to the morphological evolution of In-films at low temperatures (130–200 K) [15, 16, 18] as observed by TEM during growth. A combined TEM and x-ray study for Ag growth at slightly elevated temperatures (320–570 K) yields the following results [23, 25]: (i) the initial grain size is set by the nucleation density; (ii) grain growth starts by coalescence of grains due to contact upon growth; (iii) after film closure the average grain size increases by normal and abnormal grain growth; (iv) impurities (i.e. a higher background pressure during growth) impede normal grain growth.

While we will confirm the main features described in these previous studies, our STM results and additional observations allow a deeper understanding of the relations between the different growth stages and their link to underlying elementary processes. We report new findings related to trench formation prior to film closure, to the link between film roughness and film closure, to the annealing behavior prior to and after film closure, to the relation between GB migration and film formation status, and to facet formation.

2. Experimental

The experiments are performed in a home-made variable-temperature STM apparatus with a base pressure below 1 × 10⁻¹¹ mbar equipped with a mass selected, differentially pumped ion source, Ag evaporator, high-energy electron diffraction (RHEED) and a load-lock system for the Si samples.

For substrate preparation a Si(001) sample is degassed overnight at 900 K. After cooling down to restore the background pressure the native oxide is removed by flashing the sample to 1500 K resulting in a (2 × 1) reconstructed Si(001) surface. Subsequently, the surface-near layer is amorphized by a fluence of 1.5 × 10¹⁵ ions cm⁻² 4 keV Ne⁺ ions with normal incidence onto the Si surface at 300 K. After the ion bombardment the sample is gently annealed at 800 K for 180 s to avoid substrate modifications during the film-annealing experiments. The such prepared samples exhibit no RHEED diffraction pattern and only diffuse background on the RHEED screen. Thus the amorphous surface-near layer has a thickness larger than 1 nm. The rms-roughness of the amorphous layer is 0.2 nm. The inset of figure 2(a) shows an STM topograph of the amorphous substrate. The reproducibility of the substrate preparation method was checked several times.

The Ag is deposited by thermal evaporation on the Si amorphous layer at 300 K with a deposition rate of 8 × 10⁻³ nm s⁻¹, if not stated otherwise. The film thicknesses  \( d \) ranges from
Figure 1. STM topograph of a discontinuous film with a thickness of 1 nm after performing a linear scratch with the tip. Image size = 300 nm × 150 nm.

0.13 to 50 nm. The standard deposition temperature corresponds to a reduced temperature of 0.24T_m, where T_m is the Ag melting temperature. Even for long deposition times, the pressure during deposition remains in the low 10^{-10} mbar range, ensuring the growth of clean films free of kinetic limitations due to impurities.

After growth the films are analysed in situ at 300 K by STM. Quenching the films to temperatures below 180 K prior to imaging shows no noticeable morphological differences. The STM images are grey-scale topographs with an edge enhancing matrix filter applied to make steps better visible for representation, except for the image of figure 8 which is a differentiated topograph that appears as if illuminated from the left. Thin Ag films can be locally removed from the substrate by scratching the sample with the STM tip, as shown in figure 1. Analysis of the profiles across the resulting holes allows an estimate of the film thickness and thus the deposition rate, which is consistent with the one obtained from x-ray reflectometry (see below).

After STM imaging some of the samples are removed from the UHV system via the load-lock system for x-ray or TEM analysis. X-ray reflectometry is used to determine and control the deposition rate of the evaporator using films of thicknesses larger than 10 nm. For x-ray texture analysis the Philips X-pert diffractometer is calibrated and the samples are carefully aligned. The following types of XRD measurements were performed: \( \theta / 2\theta \)-scans, pole figures and for quantitative texture analysis cuts through the central pole figure peak (\( \omega \)-scans).

For two samples with thicknesses of 2.7 and 20 nm, TEM measurements were performed. For sample preparation, a thin carbon coating was deposited on top of the samples. Scratching the samples and inserting them into diluted fluoric acid made it possible to detach chips of the carbon film with the adherent Ag film from the Si-substrate. The analysis of electron diffraction patterns also allowed qualitative conclusions on the Ag film texture.

3. Results

Figure 2 displays STM topographs of the evolution of the Ag film morphology as a function of the film thickness. We distinguish three different regimes: (i) the nucleation and island growth regime for film thicknesses \( d \) smaller than 0.8 nm (figure 2(a)); (ii) the island coalescence regime for 0.8 nm \( \leq d \leq 10 \) nm (figures 2(b)–(d)); and (iii) the continuous film regime for \( d > 10 \) nm (figures 2(e) and (f)). To be precise we define as an island an Ag object on the substrate, which is
Figure 2. STM topographs of Ag films deposited at 300 K with thicknesses of (a) 0.3 nm, (b) 1.0 nm, (c) 2.7 nm, (d) 8.5 nm, (e) 15.9 nm and (f) 30.0 nm. Image size = 160 nm × 160 nm. The inset in (a) shows an STM image (60 nm × 60 nm) of the amorphous substrate, and in (b), a line scan between the arrows in the topograph, which reaches down to the substrate. The circles in (b) enclose islands with GBs.
not connected to another Ag object (i.e. an island may contain GBs). Island growth refers only to the growth of single-crystal islands but not to island extension by coalescence.

Figure 2(a) exemplifies the surface morphology in the nucleation and island growth regime. Superimposed on the substrate roughness, the surface is covered uniformly by small bright protrusions, which correspond to Ag islands. The density \( n_i \) of these islands remains roughly constant around \( n_i \approx 0.05 \) islands \( \text{nm}^{-2} \) up to \( d = 0.8 \) nm. An accurate count is difficult as small islands on the amorphous surface are hard to distinguish from the substrate roughness. Since Ag nuclei are crystalline and \( n_i \) is roughly constant in this regime, each island corresponds to a three-dimensional single crystal and thus GBs are not present in the islands.

The island coalescence regime visualized by figures 2(b)–(d) is defined by a continuous decrease in Ag island density \( n_i \) down to almost zero. We observe that the island coalescence regime is divided into two stages. During the first stage with \( 0.8 \text{ nm} \leq d < 2 \text{ nm} \), the island density \( n_i \) decreases by about an order of magnitude: from \( n_i \approx 0.05 \text{ islands nm}^{-2} \) for \( d = 0.3 \) nm (figure 2(a)) via \( n_i = 0.02 \text{ islands nm}^{-2} \) for \( d = 1.0 \) nm (figure 2(b)) to \( n_i = 0.007 \text{ islands nm}^{-2} \) for \( d = 1.64 \) nm (not shown). The resulting islands conserve isotropic in-plane shapes and smooth profiles. These results agree with the observations by TEM in [23, 24]. The dark and sharp lines between islands in figure 2(b) are identified as trenches that arrive down to the substrate. Trenches separate islands from each other. The identification of the dark and sharp lines as trenches reaching down to the substrate is based on our annealing experiments described below, our own TEM measurements and previous TEM experiments for Ag films [23, 24] and In films [16, 18]. Also the observation that our scratching experiments (compare figure 1) leave most islands in the vicinity of the scratch unchanged agrees with this assignment. Due to its finite size, in most of the trenches the STM tip is not able to reach the substrate. However, in some wider holes, bare substrate areas are observed, such as that between the arrows in figure 2(b).

A line scan through the area is shown as an inset in figure 2(b). In this kind of hole, the average of the contact angles (the angles between the island surface next to the substrate and the average substrate plane) has been determined to be about \( 20^\circ \) with large scatter. In the first stage of the island coalescence regime, we observe that only a few islands contain faint dark lines after coalescence, such as those encircled in figure 2(b). Below we demonstrate that these weak lines within these islands correspond to GBs. Thus, most of the islands contain no GBs and the island density decreases, as the result of a complete island coalescence. In this stage the majority of the islands are still single crystals. Initial complete coalescence was also found in previous in situ TEM studies [16, 18, 24].

During the second stage of the island coalescence regime with \( 2 \text{ nm} \leq d \leq 10 \text{ nm} \), \( n_i \) decreases mainly due to incomplete coalescence. The island density decreases in this regime from \( n_i = 0.005 \text{ islands nm}^{-2} \) at \( d = 2 \) nm to \( n_i \approx 0 \) at \( d = 10 \) nm, where the film is percolated and closes. The resulting islands are of irregular, meandering in-plane shape and are separated from each other by narrow, deep trenches (dark lines in the STM images, figures 2(c) and (d)). The surface of the islands is interspersed with weak lines which indicate the presence of GBs. Occasionally steps also give rise to lines that are, however, usually straight lines. As apparent in the inset of figure 3(c) which corresponds to this stage, during the island coalescence regime grains start to develop small facets. The irregular in-plane island shape and the presence of GBs within islands indicate that, due to the growing size of the islands, diffusion becomes too slow compared to the experimental time scale set by the deposition rate to reshape islands to compact structures and to remove the GBs. Based on scaling arguments, one expects an increase of the reshaping time with the fourth power of the linear dimension, if surface diffusion prevails [26].
Figure 3. Schematic side-view representation of Ag film growth regimes (see text). T and GB point to trenches and GBs, respectively. The STM topographs in the insets are obtained from films with thicknesses of (a) 0.3 nm, (b) 1.0 nm, (c) 5.4 nm and (d) 30.0 nm. Image size = 100 nm × 100 nm.

The simultaneous loss of compact island shape and of the single crystal property indicates that, in the first stage of the *island coalescence regime* both processes are driven by surface diffusion. Although the growing islands develop an increasing number of GBs originating from incomplete coalescence, also in the second stage of the *island coalescence regime* some grain growth is observed. Compare for instance the mean grain diameter of ∼15 nm in figure 2(c) \( (d = 2.7 \text{ nm}) \) with the mean grain diameter of ∼20 nm in figure 2(d) \( (d = 8.5 \text{ nm}) \). Contact angles increase in the second stage of the *island coalescence regime* to an average of about 30°.

Characteristic morphologies in the *continuous film regime* are shown in figures 2(e) and (f). For \( d > 10 \text{ nm} \) the island structure is lost and no more trenches are visible. The film is closed and the substrate is completely covered by a continuous Ag film. Remarkably, the continuous film surface is dominated by atomically smooth facets. From the predominant 60° and 120° boundary angles of the facets it is evident that most of them are \{111\} facets. From the comparison of
As all large grains expose \{111\} facets, it must be concluded that abnormal grain growth proceeds in the continuous film regime. Abnormal grain growth is the growth of a specific grain type at the expense of others. In the present case we speculate that it is driven by a lower surface and/or interface energy of the \langle 111 \rangle oriented grains (see below).

A summary of the morphology evolution is sketched in figure 3: in the nucleation and island growth regime single-crystal islands nucleate and grow three dimensionally on the amorphous substrate (figure 3(a)). In the first stage of island coalescence regime mainly complete coalescence takes place leading to larger, compact, single crystal islands. Trenches (T) start to develop between islands (figure 3(b)). In the second stage of the island coalescence regime island coalescence is incomplete. Polycrystalline islands with numerous GBs develop which exhibit irregular, meandering in-plane shapes separated by deep trenches (figure 3(c)). In the continuous film regime trenches are absent and large \{111\} faceted grains emerge (figure 3(d)). Representative STM topographs of each regime or stage are shown as insets of the corresponding figures.

The interpretation of the weak lines within islands as locations of GBs is substantiated by the inset of figure 3(c). In the white rectangle of the inset, several \{111\} facets are enclosed. They have angles with respect to each other which imply that they do not belong to the same fcc-crystal, but to different grains. In the white circle of the inset, a \{111\} facet with a triangular boundary and a \{100\} facet with a square shaped boundary are visible (both facets are marked by black lines). As both facets are close to parallel to the average surface plane, evidently they indicate different grains in one island.

Figure 4(a) quantifies our above discussion on the evolution of islands and grains with \(d\). The island density \(n_i\) (full squares in figure 4(a)) decreases from its constant value of \(n_i \approx 0.05\) islands nm\(^{-2}\) in the nucleation and island growth regime down to \(n_i \approx 0\) at the end of the island coalescence regime. Although it is hardly possible to obtain full grain size distributions from the STM topographs, we characterize the grain size evolution by the maximal grain size (averaged over the five largest grains) out of an ensemble of \(\approx 200\) grains. Although this characterization is subject to considerable uncertainties, clear trends are visible in figure 4(a).

**Figure 4.** (a) Island density \(n_i\) (full squares) and maximal grain size (full circles) as function of film thickness \(d\). Maximal grain size is the average of the 5 largest grains out of an ensemble of about 200 grains. (b) Evolution of the film roughness \(\sigma\) (full squares) and feature size \(\lambda\) (full circles) as a function of the film thickness \(d\) (see text). Lines to guide the eye.
As apparent in figure 4(b), initially $\sigma$ only marginally.

For quantitative analysis of the distribution of the level in the 30 nm pole figure was considerably lower than in the 14 nm one, indicating a more correspond to out-of-the-plane $\beta$. Thus takes place in the late stage of the island coalescence regime.

Additional quantitative information on the morphological evolution is provided by the dependence of the rms-roughness $\sigma$ and the height–height correlation function $G(\vec{r})$ on $d$ [27]. As apparent in figure 4(b), initially $\sigma$ strongly increases with $d$: the film grows thicker while the trenches still reach down to the substrate. In the second stage of the island coalescence regime, $\sigma$ reaches a maximum for a crossover $d_c$ around 10 nm. With film closure the trenches are eliminated from the morphology and $\sigma$ drops slightly. Further thickening of the film influences $\sigma$ only marginally.

Based on the radially averaged height–height correlation function $G(r) = \langle G(\vec{r}) \rangle_{\vec{r}=r}$, we define a characteristic lateral feature size $\lambda = \frac{1}{2}(\lambda_1 + \lambda_2)$, where $\lambda_1$ and $\lambda_2$ are defined as $G(\frac{\lambda_1}{r}) = 0$ and $G(\frac{\lambda_2}{r}) = G(0)/2$, respectively. As shown in figure 4(b), a crossover in the increase of $\lambda$ with $d$ takes place around the same value $d_c$ as for $\sigma$. Note that in the nucleation and island growth regime as well as in the first stage of the island coalescence regime, $\lambda$ is determined by the trench separation. In the continuous film regime, $\lambda$ is largely determined by the typical facet dimension. A crossover from $\lambda$ being determined by trenches to $\lambda$ being determined by facets thus takes place in the late stage of the island coalescence regime. Thus $\lambda$ as obtained from $G(r)$ is a convolution of island separation and grain separation.

From the fitting of the log–log representations (not shown), we derive exponents of power-law relations for both parameters $\sigma \sim d^\beta$ and $\lambda \sim d^\delta$ within limited ranges of $d$ and a crossover of $d_c = 10$ nm. The estimated exponents are $\beta_1 = 0.89 \pm 0.06$ and $\delta_1 = 0.8 \pm 0.3$ for $d < d_c$; $\beta_2 = -0.02 \pm 0.11$ and $\delta_2 = 0.25 \pm 0.15$ otherwise.

A decisive property in the morphological evolution of a thin film is the degree of orientation ordering of its grains. As has been pointed out in the introduction for Ag, a change from an initial random orientation to a (111) texture is expected. We performed XRD measurements in Bragg–Brentano geometry ($\theta/2\theta$-scans) for films with thicknesses of 5.4, 6.8, 14 and 30 nm. For the two thickest films, clear Ag peaks at the location for diffraction by {111} planes parallel to the substrate surface are visible indicating strong {111} out-of-plane texture. At the locations for diffraction by {100} planes just a slight intensity increase above the noise level is observed. For the thinnest films still intensity just above the noise level is observable at the {111} location.

X-ray texture analysis was carried out subsequently for the samples of 14 and 30 nm. Consistent with the $\theta/2\theta$-scans, pole figures with the Bragg condition set for the Ag {111} planes exhibit a strong central peak, and a ring of intensity at a polar angle of 70.5°. This pattern corresponds to out-of-the-plane {111} texture and the absence of in-plane order. The background level in the 30 nm pole figure was considerably lower than in the 14 nm one, indicating a more complete alignment of the grains. For quantitative analysis of the distribution of the {111} directions of the grains around the substrate normal, cuts through the pole figures are displayed in figure 5(a), where the intensity is plotted as function of the angle $\omega$ between substrate and x-ray beam. The full width at half maximum (FWHM) decreases from 10° for $d = 14$ nm to 8° for $d = 30$ nm. These values and the decrease are consistent with the distribution of the {111} facet orientations visible in figures 2(e) and (f) (see also below).

To shed additional light on the morphological evolution, plan view TEM micrographs and electron diffraction patterns of selected Ag films were taken. Figure 5(b) shows a plan-view TEM image of the 20 nm thick film shown in the STM topograph of figure 5(c). The STM topograph
Figure 5. (a) X-ray $\omega$-scans for 14 nm (lower curve) and 30 nm (upper curve) thick Ag films (see text). The FWHM of the $\langle 111 \rangle$ Ag grain orientation with respect to the surface normal decreases from 10° for $d = 14$ nm to 8° for $d = 30$ nm. The precision of the alignment and the high integration time are visualized by the presence of a small and narrow extra peak superimposed at the maxima of the Ag diffraction intensity due to the specular reflectance of the x-ray beam. (b) Plan-view TEM image and (c) corresponding STM topograph of a film with a thickness of 20 nm (image size $= 195$ nm $\times$ 195 nm).

and TEM micrograph exhibit similar sized and shaped grains. A large number of twins within the grains are visible in the TEM image. The Ag film in the ex situ TEM micrograph of figure 5(b) shows holes, which are inconsistent with the corresponding in situ STM image. It must be concluded that due to the ex situ nature of the TEM measurement (the sample was exposed to ambient between the STM and the TEM measurement) and/or due to the sample preparation, the Ag film partly agglomerated [28, 29] or detached prior to TEM imaging. Thus care has to be exercised when conclusions related to the morphological status of Ag films are drawn on the basis of ex situ TEM images (e.g. compare [30]). Electron diffraction patterns of the two films taken in the TEM are indicative of the absence of texture for the 2.7 nm film, while a $\langle 111 \rangle$ texture can be deduced from the intensity of the diffraction rings for the 20 nm thick Ag film.

In the following, we describe as the last part of the present section a number of annealing experiments which will form an important basis for the understanding of the mechanisms relevant during the film formation. The first annealing experiment demonstrates the presence of grain growth and specifically of abnormal grain growth in the continuous film regime at 300 K in a drastic way. First a 100 nm thick film was deposited at 210 K. The STM topograph of this film taken at 210 K and represented in figure 6(a) shows regular sized grains with a diameter of about 12 nm. Apparently the film has a columnar structure with in-plane grain sizes much smaller than the vertical grain sizes. The grain surfaces are rounded and not faceted. Upon annealing at 300 K for 15 h before imaging, the morphology changes as visible in figure 6(b). Due to annealing at 300 K, grains with extended facets developed. The largest visible facets with diameters of up to 80 nm are unequivocally $\{111\}$ facets as obvious from the 60° and 120° angles of their boundaries. Thus, $\langle 111 \rangle$ oriented grains grow preferentially during the annealing process. This result strongly supports our interpretation that the reduction in the number density of grains visible at the surface takes place through grain growth (i.e. GB migration) rather than through an evolutionary selection principle or lateral overgrowth [31].

The second set of experiments investigates the differences in the film annealing behavior in the island coalescence regime (film with trenches) and the continuous film regime (film without
Figure 6. STM topographs of a 100 nm thick Ag film grown at 210 K (a) and then annealed at 300 K (b). Scanned area = 175 nm × 175 nm.

trenches). Figure 7 shows in (a) an STM topograph of an 8.5 nm thick film grown at 300 K and in (b) the same film after annealing at 400 K for 120 s. The following changes took place due to annealing: (i) the roughness increased from 2.1 nm up to 4.3 nm (compare height profiles of figure 7(c)); (ii) the average grain size increased; (iii) the islands became more compact and large gaps displaying the substrate open; (iv) the contact angle of the islands with the substrate increased from an average around 30° to a value around 50°. Apparently, due to the enhanced surface diffusion by the temperature increase, the system seeks to minimize its energy by compacting the island shape, removing GBs by grain growth and increasing the contact angle to approach the equilibrium value. Surprisingly, neither the island density decreased nor the texture improved during annealing. By analysing the facet type and orientation as well as the fraction of the surface area related to faceted grains, we find that the \{111\} facet orientation distribution presents an average value of 12° for figure 7(a) and of 15° for figure 7(b). Also the area fraction associated with these oriented grain does not increase and remains around 40%. These values are consistent with the XRD data.

In figures 7(a) and (b) the morphologies of a 20 nm thick film grown at 300 K are compared before and after annealing to 500 K for 120 s. The following changes took place due to annealing: (i) the roughness decreased from 2.2 nm down to 0.8 nm (compare height profiles of figure 7(f)); (ii) the average grain size increased strongly and the maximum grain diameters reach up to 200 nm; (iii) specifically the \{111\} faceted grains grew in size; (iv) the texture improved considerably since the average of the facet orientation distribution decreases from about 10° to about 2° after annealing (the area fraction associated with the oriented grain stays close to 100%). Apparently, due to enhanced surface diffusion abnormal grain growth took place, causing the most perfectly oriented grains of the unannealed film (with their \{111\} planes most parallel to the average substrate surface) to grow laterally at the expense of all other grains. Surprisingly, surface diffusion did not cause a break-up of the film. Break-up of a non-wetting (contact angle larger than zero) film upon annealing is a well known phenomenon. Film dewetting or agglomeration is initiated by GB grooving to equilibrate surface and GB energies [32]. Once grooves reach down to the substrate, islands are present, and a scenario as discussed above for a film with trenches (figures 7(a) and (b)) would apply. Agglomeration of continuous Ag films on SiO$_2$ is initiated in the temperature range between 700 K and 900 K [28, 29]. As visible in figure 7(e), no indications of grain grooving are visible here after annealing to 500 K. In contrast, the large terraces of the \{111\} faceted grains in particular extend without steps to the edge of the grain. In the following
Figure 7. STM topographs of Ag films before and after annealing (see text): (a) 8.5 nm thick film grown at 300 K and (b) additionally annealed at 400 K; (d) 20 nm thick film grown at 300 K and (e) additionally annealed at 500 K. Image size = 380 nm × 380 nm. Height profiles between the white arrows shown in the topographs: (c) for the 8.5 nm thick film shown in (a) and (b); (f) for the 20 nm thick film shown in (d) and (e).

section, the kinetic limitation hindering grain grooving and the question why abnormal grain growth takes place only in the continuous film upon annealing will be analysed in more detail.

A striking feature of the continuous films is the presence of screw dislocations in the large ⟨111⟩ facets. Figure 8 displays an STM topograph of a Ag film with a thickness of 16.4 nm. The points of intersection of the dislocations with the facet surfaces are highlighted by white arrows. Dislocations are detected in many grains and in some cases we find several dislocations within the same grain. Their presence indicates plastic deformation of the Ag film in reaction to film stress. In fact, the presence of tensile stress in this thickness range has been reported several times for Ag [8, 9, 30]. Also visible in figure 8 are several step-like features ⟨111⟩ facets, but absolutely straight and within the grains (black arrows). These straight lines are indications of twins and slips on ⟨111⟩ inclined by 70.5° with respect to the facet. This result is consistent with the frequent twin contrast in the TEM images (figure 5(b)).
4. Discussion

In a single phase polycrystalline film the total energy $E_t$ is composed by four different contributions: the interface energy $E_i$, the surface energy $E_s$, the GB energy $E_{GB}$ and the strain energy $E_\epsilon$; such that

$$E_t = E_i + E_s + E_{GB} + E_\epsilon.$$  \hspace{1cm} (1)

Note that each energetic term has a complex dependence on the film morphology. $E_s$ for instance sums over the contributions of all grains and each contribution is a surface integral of the orientation dependent specific surface energy over the grain surface and depends evidently on grain orientation and surface area.

For a non-wetting deposit energy minimization would result in the agglomeration of the entire film into a single, monocrystalline island. The shape of this island would be a truncated three-dimensional equilibrium island shape with an orientation and contact angle determined by the surface and interface energy balance [33]. In fact, the equilibrium shapes of Au and Pb were prepared by annealing of films on a non-wetting substrate [34]. Under thin film deposition conditions the large difference in chemical potential between the phases allows atoms to populate metastable positions, in which they are either trapped or escape to lower energy positions depending on the kinetic barriers (activation energies) involved and the time available. Analysing the morphology in view of the extent to which energy minimization has been possible during growth, gives a clue to the relevant kinetic barriers.

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Our measurements give essentially no information on the nucleation stage of film formation and thus we have to give an educated guess. Ag grows on Si(001) and Si(111) in a Stranski–Krastanov growth mode forming first a wetting Ag monolayer prior to three-dimensional island formation [35]–[38]. It is thus likely that for the amorphous Si surface a disordered Ag layer or a mixed Ag/Si layer is also formed to minimize the surface free energy prior to the formation of Ag crystallites.

Once the formation of the wetting layer is completed, three-dimensional Ag crystallites nucleate on the substrate. From our own measurements we cannot derive strong conclusions on the orientation of the initial nuclei. Taking together TEM measurements, facet analysis and the annealing experiment, our results indicate that initially there is no or only poor alignment of the island crystallography with respect to the substrate. Based on energy minimization, one might expect that ⟨111⟩ oriented grains are formed preferentially as they should minimize interface and surface energy.\(^5\) However, one should keep in mind that the substrate possesses a considerable roughness on the atomic scale (maximum height difference of 0.6 nm) making the formation of a well defined facet at the interface impossible. Complementary, due to their global shape of a hemispherical cap, islands include different surface orientations, averaging over directions of lower and higher surface energy. Thus the total surface energy will also only weakly depend on the grain orientation. Therefore the formation of poorly or even randomly orientated islands appears likely in agreement with results of previous studies [16, 18, 23].

During the growth of the nuclei, initially most of the material is adsorbed on the wetting layer and diffuses to the islands, while only little Ag is deposited directly onto them (schematics in figure 9(a)). Thus, due to the kinetics of material supply, islands grow laterally and their contact angle with the substrate is below the equilibrium value.

The rapid lateral island growth will cause encounter of islands. Due to their small size two islands in contact will rapidly reshape to a new compact island through a sintering process driven by the minimization of surface area. At this stage GBs either do not form (as material is transferred rapidly from one island to the other) or rapidly migrate out. Silver surface self diffusion is rather efficient at room temperature and processes like step fluctuations, monolayer island decay and coalescence are well known [43]–[47].

As the growth proceeds, the average island size increases and surface diffusion becomes too slow compared to the experimental time scale set by the deposition rate. Islands can no longer be reshaped to compact structures and GBs can no longer be removed entirely. As pointed out already above, one expects a strong increase of the reshaping time with the linear dimension [26]. The simultaneous loss of compact island shape and of the single crystal property indicates that in the first stage of the island coalescence regime both processes are driven by surface diffusion.

One striking feature in the morphological evolution is the formation of the trenches between large irregular, often sausage-like islands, which has been observed also for other systems [16, 18, 24]. Trenches were observable for more than half of the deposition time prior to film closure, but the authors were not aware of a plausible kinetic explanation for their existence.

These deep trenches are reminiscent of the deep grooves separating mounds in homoepitaxy [48]. In homoepitaxy groove formation is due to the Zeno effect [49], which is a kinetic effect related to the step edge barrier impeding closure of narrow gaps between mounds. We believe that a similar mechanism is operative here during Ag thin film growth, although a step edge

\(^5\) The fcc(111) surface is generally measured and calculated to have the lowest surface free energy [39]–[42]. The anisotropy of surface free energy is however lower than estimated from bound counting models and amounts to 5–15%.

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Figure 9. Schematic and coarse grained side view sketches of the surface morphology in (a) the nucleation and island growth regime and (b) the second stage of the island coalescence regime. Ag islands are grey. The dashed lines indicate the equilibrium shape with larger contact angles. The width of the arrows symbolises the magnitude of material supply directly on to the Ag islands and from the island free area. The labels 0 and $x_0$ are explained in the text.

barrier is not necessarily involved. As shown in figure 9(b), after the first coalescence events the material supply to the polycrystalline islands is primarily through deposition onto the islands. Due to the small area associated with it, only little material is deposited into the trench between the islands. If we assume that all material arriving on the Ag islands remains on them, the trench can only be closed by the material arriving in the trench. If we assume the material arriving in the trench to arrange in the form of a connecting monolayer, it is straightforward to calculate the time for the formation of this monolayer. This time is apparently identical to the time the monolayer needs to grow from the right island in figure 9(b) (position $x_0$) to the position zero in the centre of the trench (assuming for simplicity identical growth behavior for the left and right island). The step position varies as

$$x(t) = x_0 e^{-Ft}, \quad (2)$$

where $F$ is the deposition rate measured in atomic layers per unit time. It is thus evident that according to (2) the closure time is infinity in this ideal situation, i.e. the trench never closes (as the Achilles will never overtake the turtle in the paradox of Zeno of Elea). Note that (2) does not take into account the finite size of the atoms nor diffusion induced fluctuations.

The assumption that no material deposited onto the Ag-island will be used to fill the gap appears not stringent. Two arguments support it. Firstly, islands are locally hemispherical caps and thus contain plenty of steps. While diffusion is rather rapid on facets, atoms incorporated into steps hardly leave them again on the time scale of the experiment. Secondly, the contact angle is still considerably beyond the equilibrium one. Therefore, for particles arriving on the Ag island, but at its edge, there is a net energetic driving force for motion towards the island centre.

For the atoms deposited into the trench a similar additional kinetic and energetic argument may be used. The more narrow the trench is, the fewer atoms arrive per unit time and length at the island edge. Thus, the more time these atoms have to follow the energetic requirement of increasing the contact angle prior to stable incorporation on the trench level by additional atoms arriving in the trench. Therefore also the atoms arriving in the trenches are likely to become incorporated into the Ag islands without contributing to trench closure. In conclusion, these considerations explain the surprising kinetic stability of the trenches, before they eventually close by fluctuations of the film growing thicker and thicker.
To discuss texture evolution and the *continuous film regime*, it is useful to analyse first in some detail the annealing experiments visualised in figure 7. The strikingly different annealing behaviour of the discontinuous and the continuous film in figure 7 will give us some clue as to why abnormal grain growth becomes so relevant once the film is closed.

As noted in the previous section, upon annealing the discontinuous film (figures 7(a) and (b)) more compact islands develop with larger contact angles and fewer, larger grains. As stated, texture does not improve by annealing. Why does texture not improve although all other changes (fewer grains, larger contact angle, more compact islands) indicate that enough diffusion is present to allow the system to develop into the low-energy direction? The answer is simple: after annealing the hemispherical cap—approximating the island surface—covers a solid angle of more than 2 sr (the average contact angle is around 50°). Thus, due to symmetry all low index orientations are present in the island surface. In other words, the island orientation does not matter. The island is always able to develop low index facets and therefore the surface energy depends only marginally on the orientation. As islands do not nucleate highly oriented, it is evident that the interface energy is not highly orientation dependent (most likely due to the microscopic substrate roughness). Therefore annealing a discontinuous film involves grain growth but not or only to a small extent abnormal grain growth.

The situation is different for a continuous film. Upon annealing (figures 7(d) and (e)) the film develops larger grains, which are much better oriented with respect to the substrate as discussed quantitatively in the previous section. As the initial film is closed and faceted, its surface contains a single low index facet (typically a {111} facet) plus some misoriented surface areas at the facet boundary. Now the film may significantly reduce its surface energy by removing grains with unfavourably orientated facets and grains with significant angles between the ⟨111⟩ direction and the surface normal by reducing the average surface energy per unit area and by reducing the surface area itself, respectively. We believe that this is the deeper reason why abnormal grain growth becomes most efficient only after film closure in the *continuous film regime*.

There is another speculation which may be added to the discussion of the annealing experiments. Although significant rearrangement of the film surface takes place, there is no indication for grain grooving which might initiate the break-up of the film. Neither do we observe the typical shape with a groove and a ridge on each side that should result from the equilibrium between the three interfaces that meet at the triple line, where a GB intersects the surface [32]. One significant kinetic barrier for grain grooving on a well oriented {111} faceted film is certainly the nucleation problem: to form grooves, material needs to be displaced from the location near the GB to the centre of the grain. However, on a {111} faceted grain the nucleation barrier is so high that the removed material will eventually return to the existing steps at the GBs. This nucleation problem is known to prevent the full island equilibration upon temperature changes even at high scaled temperatures [50, 51]. Based on this reasoning, it may be argued that to make a thin film as stable as possible against agglomeration, it has to textured as perfect as possible with the surface planes of the highest nucleation barrier parallel to the average substrate plane. This point may be relevant e.g. for heat protection coatings of windows, where as thin as possible Ag films are used for reflection of infrared radiation.

The discussion of the annealing experiment allows now also a better understanding of the grain size evolution as shown in figure 4(a). While the initial grain size increase is due to island growth and complete coalescence, with increasing lateral dimensions and increasing film thickness surface diffusion becomes less efficient and grain growth almost comes to an end. The new onset of grain growth is delayed with respect to the onset of the *continuous film regime*. 

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A similar delay is observed for faceting of the film surface: upon reaching film continuity the grain surfaces are not immediately faceted, but a few additional nm need to be deposited. Consistent with the discussion of the annealing experiments, faceted grains appear to be a precondition for abnormal grain growth. Additional more detailed experiments are highly desirable to clarify this point further.

Finally we turn to the observation of screw dislocations and twins in the continuous film (figures 5(b) and 8). Both defects are the result of plastic deformation of the thin film in response to stress. Although the evolution of intrinsic stress during deposition of thin films is still discussed controversially as mentioned in the introduction, there is agreement on a number of points. There is a consensus that in the early stages of growth during incomplete island coalescence and trench closure, the interatomic forces at the boundaries tend to close any existing gap, with the result that the neighbouring crystallites elastically deform to contact over a finite area and form a GB [52]. This mechanism, commonly referred to as island zipping, generates intrinsic tensile stress in the film and has been cited as a probable stress generation mechanism in a wide variety of materials. The elimination of GBs during grain growth has also been proposed as an origin of tensile stress, both during and after deposition [53]–[55]. Grain growth generates stresses as GBs have lower densities than the bulk material. The tensile stress generated by both mechanisms may cause nucleation of dislocations which may glide through the grains and result in slip lowering the stress and causing the observed dislocations and twins. Thus, this is an additional mechanism that should be taken into account to explain the tensile stress relaxation observed during polycrystalline film growth [8]–[14].

5. Conclusions

In the present work, STM has been shown to be a powerful tool to probe polycrystalline thin film growth. The information on the details of the surface structure (roughness, facets) together with dedicated annealing experiments allowed us to uncover new aspects in the formation of a polycrystalline thin film. Most noteworthy, we (i) give a kinetic explanation for the formation and surprising stability of trenches separating islands prior to film closure; (ii) are able to understand the evolution of grain size with film thickness and (iii) give an explanation why abnormal grain growth is initiated only when continuous films develop facets. As a general conclusion, we show that the large kinetic stability of the trenches strongly influences all the structural features during the initial growth stages, i.e., island density, grain size, roughness and texture evolution. We believe that our experiments point out a route to a new type of STM experiments, which will allow many of the remaining unsolved questions in thin film growth to be understood.

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