

Chapter 6

Influence of the substrate morphology on the organic layer growth: PTCDA on Ag(1 1 1) and Au(1 1 1)

The electrical and optical properties of organic films strongly depend on their structural and morphological properties. Ideal epitaxial growth resulting in perfect, nearly defect-free films requires optimum conditions [7]. This is particularly difficult in the heteroepitaxy of very different materials like, e.g., organic-inorganic heterostructures [8, 9]. The problem with the preparation of such systems lies in the nature of the involved substances. Whereas the structural periodicity in inorganic compounds is on the scale of few Ångström, the dimensions of organic unit cells are usually in the range of nanometers. In addition, the anisotropic shape and intermolecular interaction, the very different thermal expansion coefficients, and the (partly excited) internal degrees of freedom, e.g. the soft vibrational and phonon modes of condensed molecules may result in different structural modifications (polymorphism) in the condensed phase and in unexpected growth behavior. Thus, imperfections at the interface which extend into the growing film are foreseeable.

The potential applications of organic layers on metal surfaces may be affected by structural imperfections. This is for instance true for the charge carrier injection at the

interface and for the carrier mobility within the film which is hindered by traps and scattering at grain boundaries and defects as well as by the hopping barriers between non-equivalent neighboring molecules. Moreover, the optical properties may suffer from imperfections causing non-radiative decay channels, traps, and scattering centers for exciton transport, and they may change by varying molecular orientation, geometric structure, and film morphology as a function of organic film preparation [67].

The structural imperfections within a thin film which affect its quality and properties arise from the dynamical growth behavior and from the properties of the interface. It is of course known from many studies of inorganic materials that imperfections of the underlying substrate may deteriorate the growth and structural properties of the film. However, the details and the extent of the influence of the substrate surface quality on organic layer growth have not been systematically investigated so far, and very few experimental results are yet available. In the following paragraphs the influence of the substrate on the initial growth of an epitaxial organic film will be addressed. Emphasis is placed on the influence of the morphological properties of the metal substrate, in particular the effect of steps and step bunches on the growth behavior. In a first part we will focus on the kinetic effect of the substrate morphology on the growth. Therefore, the variation of the substrate temperature during adsorption of the molecules is discussed. Thereafter, the effects of the substrate morphology, specifically step bunches and facets, on the *horizontal* and *vertical* growth are shown for two significant examples.

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6.1 Real-time observation of organic film growth on the Ag(1 1 1) surface

The four PEEM images of figure 6.1 show the PTCDA growth on a Ag(111) surface at a substrate temperature of 378 K. These images were selected from a sequence of images recorded in real-time during deposition (acquisition time: 4 seconds per image with 2 seconds dead time corresponding to about 50 images per monolayer). The image contrast of the PTCDA layer is due to the above mentioned differences in

electron emission intensity (due to work function change and attenuation as discussed in chapter 5 on page 41). The selected surface area consists of a flat region in the center of the images and areas of high step density (step bunches) in their upper and lower part. At 0.25 ML coverage (figure 6.1.a) the step bunches on the rough surface areas appear as dark lines. This contrast is due to the decoration of steps by PTCDA molecules during the very initial growth of the first layer (below 0.04 ML) which is often termed inhomogeneous nucleation. This finding is in agreement with that of a previous STM investigation [35] which also indicated that steps may be attractive to the nucleation of PTCDA islands on the clean Ag(111) surface while they appear to be repulsive on Ag(110). From the present data it can be derived that at least not all substrate steps act as nucleation centers because of the temperature dependence discussed below, but it cannot be excluded that some islands start to grow at steps. As soon as the surface is fully covered with PTCDA (figure 6.1.b–d), the step bunches appear bright as for the clean Ag(111) surface, because the work function at the steps is smaller than on the terraces, apparently also with an adsorbed monolayer.

As clearly seen in the recorded movie [69], the first two PTCDA layers grow in an ideal layer-by-layer fashion (which is only indirectly seen in the selected snapshots of figure 6.1). Figure 6.1.a–c show the nucleation of the first three layers for nominal coverages of 0.25 ML, 1.05 ML, and 2.05 ML. The topmost PTCDA layer appears always dark in the (intensity rescaled) images. The nucleation of the second and third layer starts only after the layer underneath is fully completed. For the third layer, however, there is a competition of layer growth and 3D island formation. Thus, before the third layer is completed, 3D islands (black in figure 6.1.d) are formed (second and third layer appear light- and dark-grey, respectively). From our growth studies at different substrate temperatures, it is derived that this type of Stranski-Krastanov growth (2 stable layers, then 3D-island formation) always occurs for temperatures slightly above room temperature (7).

In the following section the nucleation site and nucleation density for the different layers is brought into focus. It is remarkable that the positions of the nucleation sites differ from image to image, indicating that the nucleation sites are not determined by spot-wise modifications of the surface morphology or by grains of contamination. Nevertheless, the substrate morphology does influence the nucleation. There is a differ-

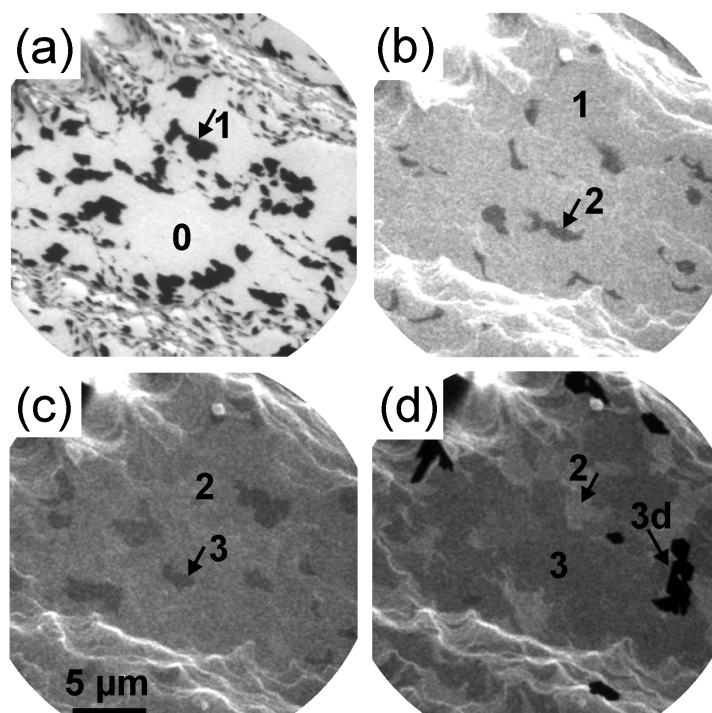


Figure 6.1: In situ observation of the PTCDA growth on a Ag(111) surface at 378 K. The UV-PEEM images (a) – (d) show the identical area on the surface for the nominal coverages of 0.25, 1.05, 2.05, and 5 ML. The field of view is $23 \times 23 \mu\text{m}^2$. Only the intensity of image (a) was rescaled to optimize the contrast. The islands with the thickest PTCDA layer appear always darker than the surrounding. The labels 0, 1, 2, 3, and 3D indicate the uncovered substrate, the first to third layer, and the 3D-islands.

ence of the nucleation densities on rough and flat areas of the substrate which is most obvious in the low coverage range (figure 6.1.a). In the rough area, the average size of the two-dimensional (2D) islands is significantly smaller than that in the smooth area (center) but their density is significantly higher. Moreover, the large 2D islands are mainly formed at the rim of the smooth area close to step bunches. At higher coverages (figures 6.1.b–d) the overall nucleation density decreases and the island size increases.

6.1.1 Temperature dependence

The substrate temperature is an important parameter for the control of the growth process. The influence is demonstrated in figure 6.2 for a low (320 K, figures 6.2.a–b) and a high temperature (403 K, figures 6.2.c–d). The figure compares the situation for the two extremes of figure 6.1, i.e., the nucleation of the first layer (0.25 ML) and the situation after formation of 3D islands (nominal 5 ML).

The overall nucleation densities for the first layer and for the 3D islands are higher at 320 K (figures 6.2.a and b) than at 403 K (figures 6.2.c and d) indicating diffusion limited formation of nuclei. The corresponding densities at 378 K (compare figures 6.1.a and d) fit in between. Note, that at 403 K the 3D nucleation density is so low, that the field of view had to be enlarged for the 5 ML coverage (figure 6.2.d). The 0.25 ML images show an influence of the surface morphology for both temperatures. In figure 6.2.a the smooth and rough areas are highlighted by solid and dashed lines, respectively. In the smooth area the 2D islands are considerably larger than in the rough areas, their density, however, is lower confirming the observation at 378 K (figure 6.1).

At 403 K the 2D islands of the first layer prefer nucleation sites near step bunches (figure 6.2.c). The same is true for the 3D islands at 403 K (figure 6.2.d). At 320 K the density of 3D islands is higher, so that nucleation also occurs on the smooth area between the step bunches. Beside the 3D islands (black in figure 6.2.b) are areas which are up to five layers thick, which can be derived from the different grey levels. At this temperature the growth mode transfers from Stranski-Krastanov to quasi Frank-van der Merwe growth [52, 70, 71, 34, 51].

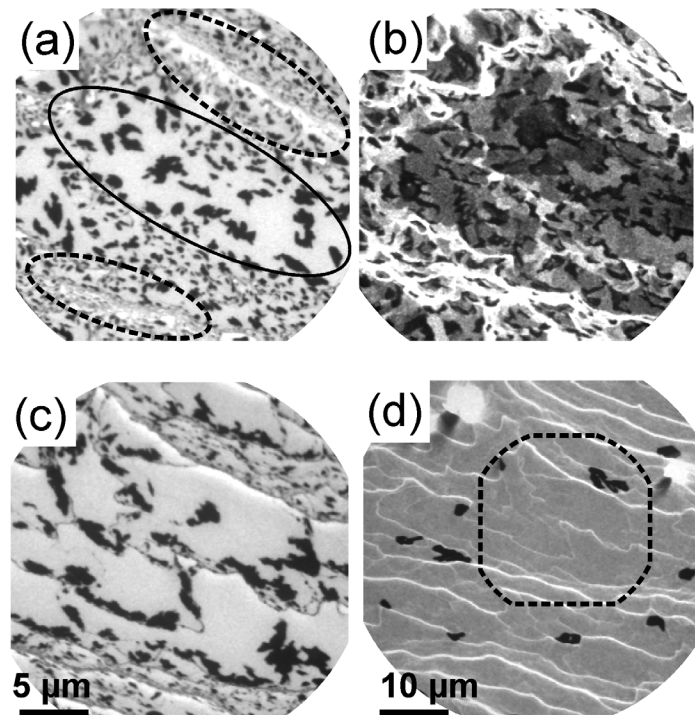


Figure 6.2: PEEM images of the PTCDA growth on a Ag(111) surface at different substrate temperatures: images (a, b): $T = 320$ K, images (c, d): $T = 403$ K. For each temperature two images from a sequence of 300 images were selected for a nominal coverage of 0.25 ML (a,c) and 5 ML (b, d), respectively. The field of view is $23 \times 23 \mu\text{m}^2$ (a-c) and $46 \times 46 \mu\text{m}^2$ (d), respectively. For the identification of the layers refer to figure 6.1. The ellipses in (a) mark high (dashed lines) and low (solid line) step density regions. The marked area in (d) corresponds to the entire area of (c).

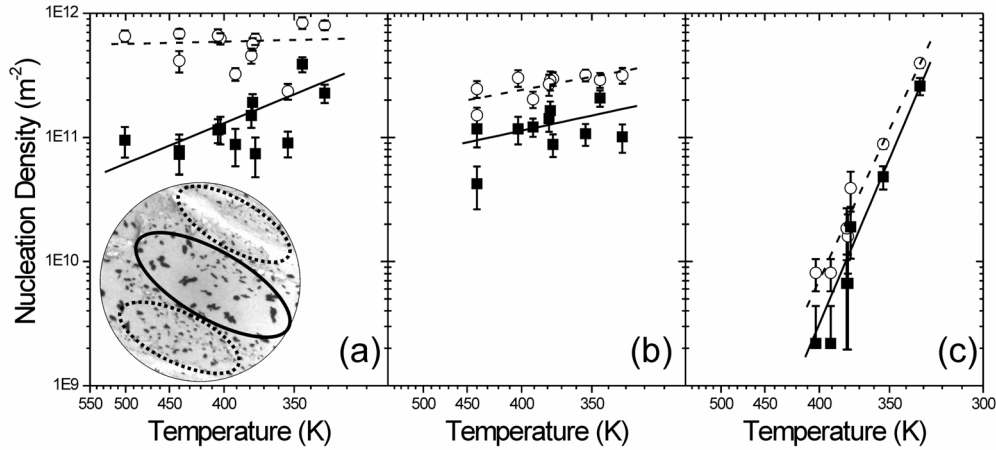


Figure 6.3: Arrhenius plots showing the temperature dependence of the nucleation densities of the first (a) and second layer (b), and for 3D islands (c). Different areas on the sample were used for the analysis. The open/full symbols and dashed/solid lines refer to substrate areas with the high/low step density, which are marked in the inset. The parameters for the exponential fit are given in Table 6.1.

6.1.2 Influence of the substrate morphology on the growth kinetics

The real time observation of the PTCDA growth was repeated for different temperatures. At specific coverages (0.25 ML, 1.05 ML and 5 ML) the nucleation density for the first and second layers and for the 3D islands were analyzed. In figure 6.3 the nucleation densities are plotted on a logarithmic scale versus $1/T$ (Arrhenius-plot) for these coverages. The open and solid symbols distinguish between rough and smooth substrate areas, respectively, as indicated in the inset of figure 6.3.a. For the first and second layer the analysis was done in a field of view of $23 \times 23 \mu\text{m}^2$ (corresponding to the magnification of the real time observation). The density of the 3D islands was determined at a lower magnification (field of view: $46 \times 46 \mu\text{m}^2$).

Assuming thermally activated diffusion during nucleation the following exponential relation has been fitted to the data (solid or dashed lines for smooth and rough substrate

areas, respectively, referring to the different ellipses in the inset of 6.3.a):

$$n_x(T) = N_0 \exp(E_n/kT) \quad (6.1)$$

where n_x is the nucleation density at temperature T , k the Boltzmann constant, E_n an activation energy for the nucleation process, and N_0 the exponential prefactor which depends on the deposition rate. The derived fit parameters E_n and N_0 are listed in table 6.1.

In general, this temperature dependence is determined by the diffusion and nucleation of the molecules. Unfortunately, up to now no sufficient theoretical description of the growth exists, which involves the specific properties of molecules like, e.g., orientation dependence, non-isotropic bonding to the neighboring molecules, cluster mobility, and internal degrees of freedom. Consequently, atomistic descriptions like those suggested by *Venables* [72] are oversimplified and can only be applied in a limited way. Under this simplifying assumption, the energy E_n can be related to the surface diffusion energy E_d and the nucleation energy E_i of a critical cluster of size i

$$E_n = p \cdot (E_d + E_i/i) \quad (6.2)$$

with $p = i/(i + 2)$ and $p = i/(i + 2, 5)$ for two- and three-dimensional nucleation, respectively. The deposition rate R dependence of the prefactor is given by $N_0 \propto R^p$. The surface diffusion constant is defined as

$$D_{\text{diff}} = \nu \exp\left(-\frac{E_d}{kT}\right) \quad (6.3)$$

with the ‘‘attempt’’ frequency ν . With the nucleation constant

$$D_{\text{nucl}} = \nu \exp\left(-\frac{E_i}{i \cdot kT}\right) \quad (6.4)$$

an effective diffusion constant can be defined as $D_{\text{eff}} = D_{\text{diff}} \cdot D_{\text{nucl}}$, so that the relation of equation (6.1) can be expressed as

$$n_x(T) \propto \left(\frac{R}{D_{\text{eff}}}\right)^p \quad (6.5)$$

In the following the so called *diffusion length* is defined as $L = 1/\sqrt{n_x(T)}$. The temperature dependence of the nucleation density of the first layer significantly differs

Table 6.1: Fit parameters N_0 and E_n for the curves of figure 6.3 describing the temperature T dependence of the island density $n_x = N_0 \exp(E_n/kT)$.

Layer	1 st layer		2 nd layer		3D islands	
	rough	smooth	rough	smooth	rough	smooth
N_0 (m ⁻²)	$10^{12.0 \pm 1.3}$	$10^{9.5 \pm 0.3}$	$10^{10.7 \pm 0.2}$	$10^{10.2 \pm 0.5}$	$10^{1.4 \pm 0.5}$	$10^{0.2 \pm 1.5}$
E_n (meV)	10 ± 10	130 ± 20	58 ± 18	70 ± 30	670 ± 40	740 ± 100

for the growth on smooth and on rough substrate areas (figure 6.3.a). On the smooth area the nucleation density has an exponential dependence indicating that thermally activated diffusion processes are involved in the nucleation process and in the subsequent growth. In contrast, the 2D island density on the rough substrate area is nearly constant over the whole temperature range of 330 K to 500 K, i.e. no thermally activated process determines the nucleation density. Thus it can be concluded that the diffusion length is limited to small areas between step bunches and is hence temperature independent. As consequence, the nucleation and therefore the growth are determined by the substrate morphology, which itself depends on the sample preparation.

The extrapolation of the two fit curves in figure 6.3.a (for flat and rough substrate areas) towards lower temperature yields a crossing point at about 300 K. Below this temperature the thermally activated nucleation density is higher than the density of substrate defects or traps (i.e. the diffusion length is smaller than the distance of traps like steps or step bunches) and therefore the growth will not be dominated by substrate morphology effects.

For the second layer the nucleation density of both, the smooth and the rough area depends on the temperature (figure 6.3.b). The slope of the fit curves results in activation energies of diffusion of $70 (\pm 30)$ meV and $58 (\pm 18)$ meV for the smooth and for the rough area, respectively, which are identical within the error bars (see table 6.1). Only the absolute value of the nucleation density is about half an order of magnitude higher for the rough area. Comparing the experimental data of the second and the first layer, the 2D island density on the rough area is significantly smaller for the second than for the first layer. Thus, expectedly the influence of the substrate morphology on the nucleation is reduced if one monolayer of PTCDA covers the substrate.

The 3D island density varies over about two orders of magnitude in the small explored temperature range of 80 K. However, the temperature dependence of the 3D island nucleation density (figure 6.3.c) differs only weakly for the two different types of surface areas. The substrate morphology also has no influence on the nucleation density, especially at low temperatures. The slope of the fit curves corresponds to an activation energy of about 0.7 eV, which corresponds well to the result of *Krause et al.* deduced from x-ray diffraction [52, 70, 71]. The activation energy is about one order of magnitude larger than for the first and second layer (table 6.1). In contrast,

for the 3D islands the pre-factor N_0 is about 9 orders of magnitude smaller than for the first and second layer. This indicates that the nucleus formation of the first and second layer differs from that of the 3D islands. This behavior of a high activation energy and a low pre-factor value was seen for the Stranski-Krastanov growth of metal on metals [72] and of metal on Si(1 1 1) [73], which can be explained by a high value of i for the critical cluster size [72], or by a mobility of smaller clusters [73].

6.1.3 Discussion

A model describing the influence of step bunches on the nucleation of 2D and 3D islands is depicted in figure 6.4. On smooth surface areas (figure 6.4.a) the lateral corrugation of the potential is equal to the activation energy of diffusion E_d . The substrate morphology at step bunches may cause either an attracting (6.4.b) or a repelling (6.4.c) potential for the diffusing PTCDA molecules. In the first case, the attractive potential offers nucleation sites of constant concentration. As long as the thermally activated diffusion length is larger than the distance between these pinning centers, the nucleation occurs only at defects and is therefore temperature independent.

The second possible case of a repelling potential at step bunches could be due to an Ehrlich-Schwoebel-barrier [74, 75] for the PTCDA molecules at steps or step bunches. As a consequence the diffusing PTCDA molecules are trapped between these barriers. In each of these trap areas which are surrounded by step bunches the PTCDA molecules diffuse until nucleation occurs. If the diameter of the smooth trap area is considerably smaller than the diffusion length only one nucleus is formed in each trap. Then the overall nucleation density is independent of the temperature and only determined by the density of traps or step bunches.

The situation changes, when a complete monolayer of PTCDA molecules covers the substrate including the step bunches. Then the height of the potential barriers at step bunches is significantly reduced for the molecules diffusing on top of the first layer. By thermal activation it is now easier for the PTCDA molecules to overcome the barrier, resulting in a temperature dependent nucleation density. Consequently, in the case of an attractive potential not every (or even no) defect (or step bunch) pins molecules or, in the case of repelling barriers, not every trap (or no) area is a center of nucleation.

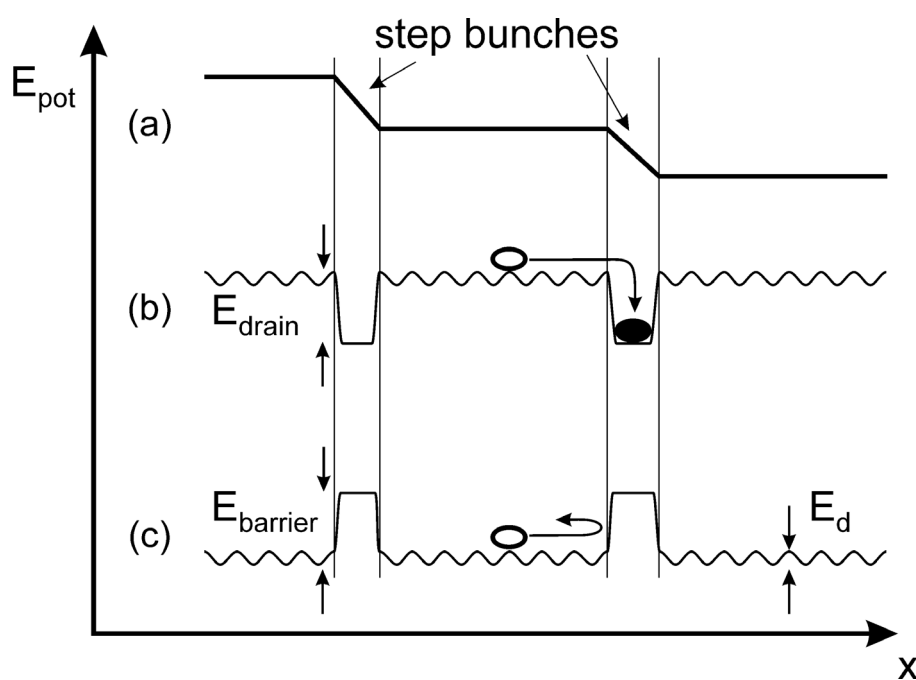


Figure 6.4: Model of the potential landscape to illustrate the influence of the step bunches on molecular diffusion. The top scheme (a) depicts a cross sectional view of a surface with two step bunches. The middle (b) and lower (c) drawing show two extreme situations for the potential which a single molecule may sense during diffusion: step bunches acting as drains (b) or barriers (c). The smooth surface has a lateral potential corrugation with the surface diffusion energy E_d . Note that the lateral corrugation of the potential is considerably smaller than the vertical potential which equals the chemical binding energy.

Of course, the same is valid for PTCDA molecules diffusing on the second layer and forming 3D islands. The molecules are less disturbed by the step bunches and are able to diffuse over long distances of about $10 \mu\text{m}$ to create 3D islands (6.2.d).

It is interesting to note that single steps which are present also on the smooth areas of the surface have much less influence than step bunches. This has been shown with LEEM experiments in chapter 5 on page 41. These clearly showed single steps also on the smooth areas in between step bunches.

6.2 Influence of the substrate on growth direction

We have carefully followed the growth of the first and second layer where the PTCDA molecules are constrained between two step bunches, about $1.7 \mu\text{m}$ apart from each other, on the Ag(111) surface as shown in figure 6.5. The growth starts by step decoration (shown at a coverage of 0.08 ML) and is followed by nucleation on the terraces. Only after the nucleus has grown to cover the whole terrace across the short side, the growth proceeds in the other direction, i.e. along the channel constrained by the step bunches as indicated by the red arrow in figure 6.5 at 0.21 ML. One of the nucleation events which is shown to occupy a $1.7 \mu\text{m}$ wide terrace across, grows (as shown by the red arrow in figure 6.5 at 0.21 ML) covering the whole length of the bounded region (0.52 ML) without any other nucleation event occurring inside this region.

The direction of the growth front¹ of the second layer, shown in the second row of figure 6.5, is opposite to that of the first layer. The front starts from the step bunch (shown at 1.04 ML) and proceeds parallel to it towards the right side of the image (see the subsequent images). From the curvature of the step bunch we conclude that the nucleation of the second layers occurs selectively on the lower side (of the step bunch).

There is an inversion of the growth direction between the first and the second layer. For the former, the growth proceeds in two distinct steps. In the first, the molecules nucleate preferentially at the steps (shown by the decorated images). Such

¹We refer to the *growth front* as the slowest evolving edge of a 2D-terrace. This is defined in a similar fashion to the growth of facets of 3D-crystals. The crystal shape is determined by the facets with slowest growth rate.

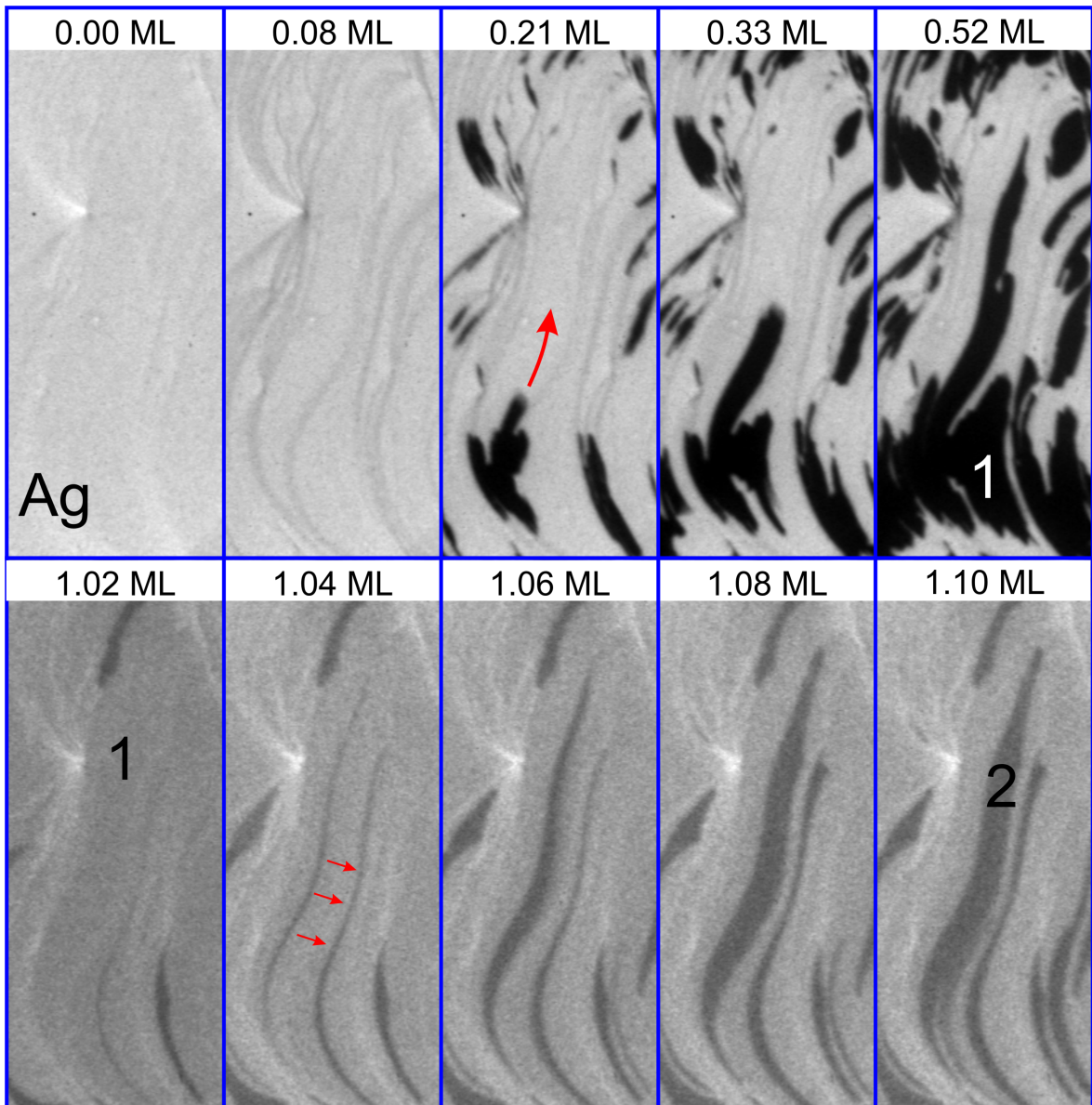


Figure 6.5: Growth direction transition: UV-PEEM images of the growth of the first two layers at 430 K. In each image the coverage is given. The thickness of the layers is marked with Ag (for the Ag(111) surface), 1 and 2. The field of view is $7.6 \times 19.4 \mu\text{m}^2$.

nucleation has been shown to form complicated structures and to induce faceting of the step bunches [76, 35]. Furthermore, we support also for these high temperatures the observation of *Glöcker et al.* [35] at room temperature that the steps attract PTCDA molecules. Only after all the available step bunches have been covered the nucleation starts on the (111) surface. The absence of a front of propagation at the steps is a first indication that the two structures, the one formed on the steps/facets and the one formed on the (111) surface, are not compatible and do not propagate from one region to the other. A closer inspection to the curvature of the growing front of images from 0.21 ML to 0.52 ML, reveals that the front evolves at the convex side. This phenomenon (comparable to that of the capillary action of liquids), is an indication of a repelling interaction between the two structures, on the (111) terrace and on the facets. This repelling effect is consistent with the lack of new nucleation events within the terrace and by the *step-limited* nucleation observed in the first monolayer regime (see the open symbols in figure 6.3.a) for regions with high step density in combination with the suggested *barrier effect* of the step bunches (shown in figure 6.4.c).

6.3 Influence of the substrate on growth mode

The growth of PTCDA on the Au(111) surface is significantly different from that on Ag(111) due to the formation of a different interface structure and bonding. The Au(111) surface is reconstructed ($22 \times \sqrt{3}$), but the overall morphology consists of terraces crossed by single steps, regions with high step bunch density, and large facets, as shown in the first images of figure 6.6.

We report in the following the effects exerted by the substrate morphology (steps, step bunches and faceting) on the growth mode, i.e. the *vertical* growth, of PTCDA on Au(111). In figure 6.6 nine images of the growth fashion are presented. Notice that the growth of the first layer proceeds in an *ideal* layer-by-layer with a higher nucleation density on the areas separated by the step bunches (red oval). After the closure of the first layer, the second layer starts. In the following a coexistence of many open layers is observed. However, we pose the emphasis on the vertical growth mode in the last image. Two regions are marked distinguishing between a highly stepped region (with facets) in the blue oval and a flat region (with single steps) in the green oval. The

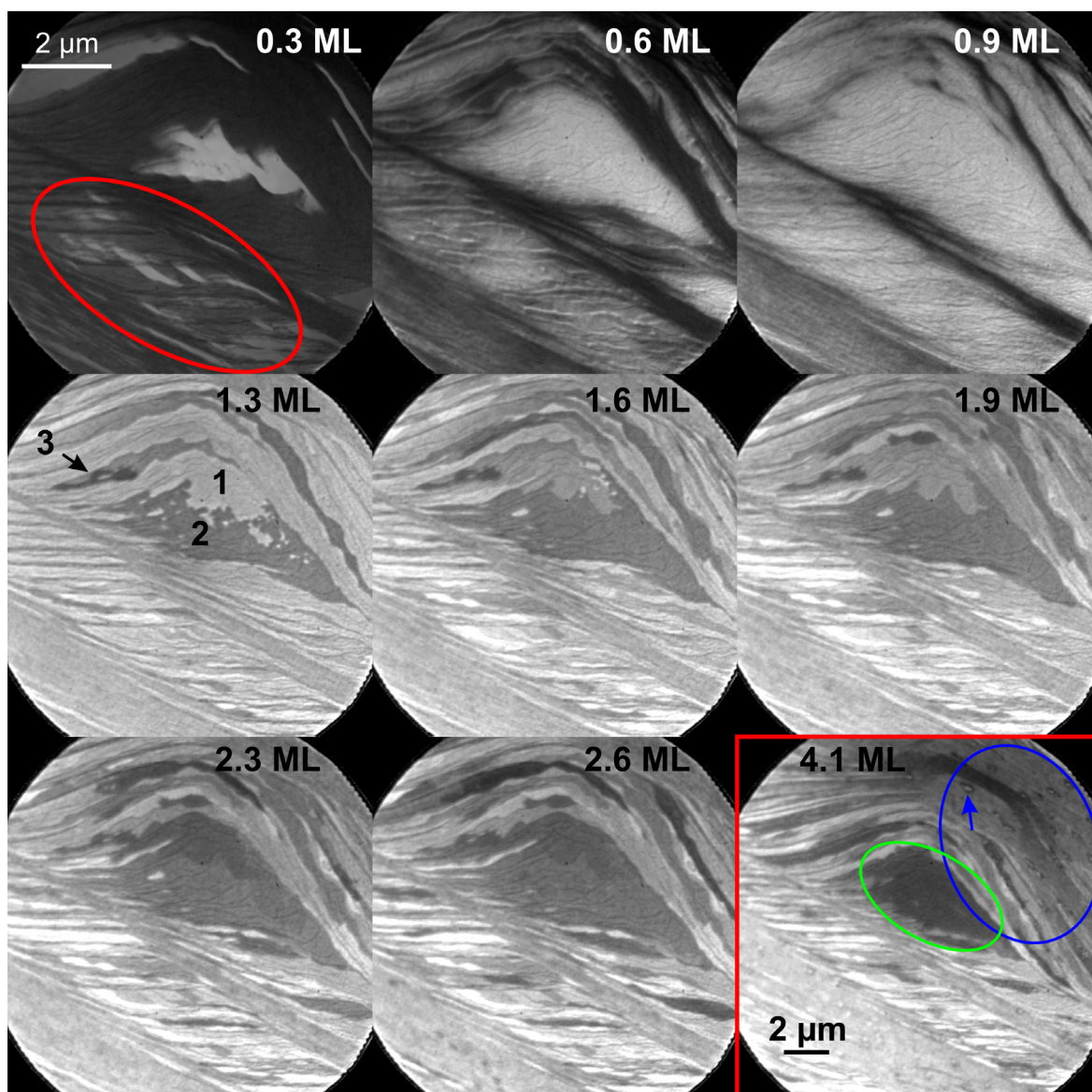


Figure 6.6: Growth of PTCDA on Au(111) at 350 K. LEEM images at 2.2 eV of the growth up to the fourth layer. Notice that the last image has a different scaling.

growth mode is different in the two regions. Inside the blue oval, i.e. a region with facet and step bunches, an arrow marks a 3D-island. Inside the green oval, the largest step-bunch-free region in the field of view, no 3D-islands is observed. In this region the growth proceeds in a layer-by-layer fashion. In contrast, in the stepped region a Stranski-Krastanov growth mode is observed [77]. These macroscopic differences, i.e. two different growth modes, can be described with a thermodynamic approach taking the surface or interface energies into account. Within this simple description, the layer-by-layer growth is obtained when the sum of the adsorbate surface energy γ_a and the interface energy γ_i is smaller than the surface energy of the substrate γ_s , i.e. when $\gamma_a + \gamma_i < \gamma_s$. The transition to the Stranski-Krastanov growth mode occurs when the energy difference $\Delta\gamma = \gamma_a + \gamma_i - \gamma_s$ inverts the sign after a few layers of deposition. The origin of the change in sign can be explained by assuming a lattice mismatch between the deposited film and the substrate. In the first layers it is therefore favorable to *wet* the substrate, whereas at some critical thickness, the lattice mismatch is compensated and the growth proceeds with 3D-island formation. It is foreseeable that there is a difference in stress on the surface of the substrate in step-free regions and in others with faceting and step bunches. Furthermore the presence of faceting can be a consequence of the surface stress. Within this model, the change in stress between the two regions is translated into a different growth mode according to the thermodynamic origin of growth modes described by *Bauer* [77].

6.4 Summary and conclusions

The presented PEEM data give first direct experimental evidence of the influence of the substrate morphology on the initial film formation in organic molecular beam epitaxy (OMBE) of PTCDA on Ag(111). Above room temperature PTCDA films grow in a (slightly modified) Stranski-Krastanov mode. The image sequence during deposition of PTCDA molecules shows a perfect layer-by-layer growth for the first two layers followed by 3D island formation. This behavior reflects the influence of the Ag(111) metal substrate on the bonding and structural properties, i.e. the strong interaction between substrate and first layer, the weaker interaction between first and second layer causing a strained superstructure of both layers with respect to the (102) β -PTCDA

bulk plane, then a slightly weaker interaction between the following layers leading to the formation of relaxed 3D islands [34].

The diffusion process of PTCDA is strongly influenced by the substrate morphology resulting in a higher nucleation density at rough surface areas. The strongest effect was observed for the nucleation of the first layer, which shows a temperature independent density above room temperature. This behavior can be explained by either attractive or repelling potential barriers at steps. The morphology effects are reduced if one monolayer of PTCDA covers the surface completely.

In a detailed example the potential barriers at the step bunches have been shown to exert a repelling potential. This is most likely due to the formation of facets at the step bunches which are covered by molecules in the very beginning of the growth. The structures formed on such facets are found to be non-compatible with the growth on the (1 1 1) surface and are acting as barriers for the molecular diffusion. The situation is reversed for the growth of the second layer which is favored at steps and only proceeds from the *lower* side of the step towards the opposite side.

In another example the effect of inhomogeneous surface tension on large terraces and terraces constrained between facets is shown to exhibit a strong influence on the growth mode according to a very simplistic picture [77].