Chapter 7

Direct observation of metastable organic layer growth: transition from Stranski-Krastanov to Frank-van der Merwe

The deeper understanding of the growth mode is of general interest for heteroepitaxy. In many cases, the growing film forms islands (Volmer-Weber or Stranski-Krastanov) but usually a closed film of constant thickness is wished. Different methods have already been developed to overcome this problem, e.g. additional adsorbates have been used, which influence the growth. These adsorbates are separated in two types - surfactant [78] and interfactant [73]. The first method is widely applied. The surfactant stays mainly at surface during the growth, influences therefore the free surface energy and the nucleation process on top of the growing film [79]. The interfactant remains at the interface during the growth and influences the free interface energy and the nucleation process of the first layer(s). Both methods transfer the growth into a layer by layer growth. The disadvantage of the surfactant method is the danger of doping the growing film by the additional adsorbate, so that they are useless for electronic devices. However, the interfactant can have a drastic influence on the electronic properties at the interface, which is unwished for many applications in electronic devices.

An interesting question remains open: why and how the Stranski-Krastanov growth

is influenced by the growth kinetics, i.e. by growth temperature and deposition rate. Other parameters like the substrate morphology are already discussed in the previous chapter. Of special interest is the organic growth on various metallic surfaces which differs to most of the atomic growth systems. The bonding of the organic molecules to the substrate (mostly chemisorption) is stronger than the intermolecular bonding in the organic film, which is usually seen as a Van-der-Waals interaction. This different kind and strength of bonding let expect different growth processes (e.g. diffusion, nucleation, misfit relaxation, crystal structure) or even the growth mechanism. A number of fundamental questions are addressed as to what can be transferred from the 'old/classical' knowledge of atomistic growth? Where are the limits? What is new in organic growth?

In this chapter we discuss the Stranski-Krastanov growth of PTCDA on the Ag(1 1 1) surface and the transition in growth mode when the temperature is lowered. This topic has been investigated the first time by a microscopic method in real time.

7.1 Temperature dependence of the PTCDA growth mode

We observed directly and in real time the growth of PTCDA on the Ag(1 1 1) surface [69]. Nine snap shots of the growth of the first five layers are shown for the temperatures 378, 354 and 320 K in figures 7.1, 7.2 and 7.3, respectively. The contrast in these images is due to the work function changes mainly of the first layer and due to the attenuation of the electrons emitted by the silver substrate (see Chapter 5). As a result the first layer of PTCDA appears darker than the silver substrate and the intensity of following PTCDA layers monotonically decreases [80]. Since the intensity strongly changes, the image contrast is optimized by rescaling after 0.9 and 1.9 ML. The labels Ag, 1 to 7, and 3D are meant to help the identification of the Ag substrate, the 1^{st} to the 7^{th} PTCDA layer, and the three-dimensional islands, respectively. The data were taken on two crystals with a different surface morphology. The surface of Fig. 7.3 had a lower density of regularly shaped substrate steps and step bunches than the surface in Figs. 7.1 and 7.2 - as subsequent LEEM investigations have shown. As a consequence the substrate step structure in Fig. 7.3 becomes visible by the half-moon (or banana)

like shape of the growing PTCDA island.

In the investigated temperature range between 320 K and 400 K, the first two layers of PTCDA grow in a quasi-ideal layer-by-layer mode: after the first layer is closed, the second layer starts growing on top and is fully completed. The growth of the following layers differs significantly from this behavior. Fig. 7.1.g shows the situation for the higher temperature (378 K) at 2.8 ML. Before the third layer is completed, the fourth layer starts and 3D islands are nucleated. This kind of growth is usually assigned to the Stranski-Krastanov growth mode [77] which has already been observed in real time e.g. at the hetero-epitaxial system Pb/Si(1 1 1)-(7x7) [73, 81]. The essential difference is that in the metal on semiconductor case the 3D islands are formed on a perfectly closed interface layer like it is predicted by a thermodynamical description [77]. In our case the 3d-islands grow on an imperfectly closed film, about 3 ML thick. Once 3D islands are nucleated at 378 K, the subsequently deposited PTCDA material is incorporated into these islands and not in the third layer. The fourth layer – existing at 2.8 ML (Fig. 7.1.g) – even disappears in this growth stage (Fig. 7.1.h-i).

At lower deposition temperatures (354 K in Fig. 7.2 and 320 K in Fig. 7.3) the nucleation density of the different layers is increased, following an Arrhenius-like behavior, and is therefore determined by the growth kinetics, involving thermally driven diffusion and nucleation processes [68]. A second change regards the vertical roughness. Whereas the first two layers show always the layer-by-layer like behavior, the subsequent growth involves more and more layers if the deposition temperature is decreased. At the intermediate temperature of 354 K, the fraction of the visible 3^{rd} and 4^{th} layer (in Figs. 7.2.g-i) is larger than at 378 K. At 5 ML (Figs. 7.2.h-i) the 4^{th} ML co-exists with the 3d-islands. At 320 K layers even with a thickness of up to 7 ML co-exist with 3d-islands (Fig. 7.3.g-i), forming a hill like morphology. This microscopic observation corresponds to the growth transition from *Stranski-Krastanov* to *quasi-layer by layer* mode already found for the PTCDA/Ag(1 1 1) system by lateral averaging methods [34, 52].

This kind of growth transition was observed for non-organic growth in the late 80s and early 90s (e.g. Ni/W(110) [82], Pb/Cu(1 1 1) [83], Pb/Si(1 1 1) [73], Ge/Si(1 1 1) [84, 78]). In these systems an ideal Stranski-Krastanov growth was observed at elevated temperatures, i.e. 3D islands on a perfectly flat interface layer. In our case, we

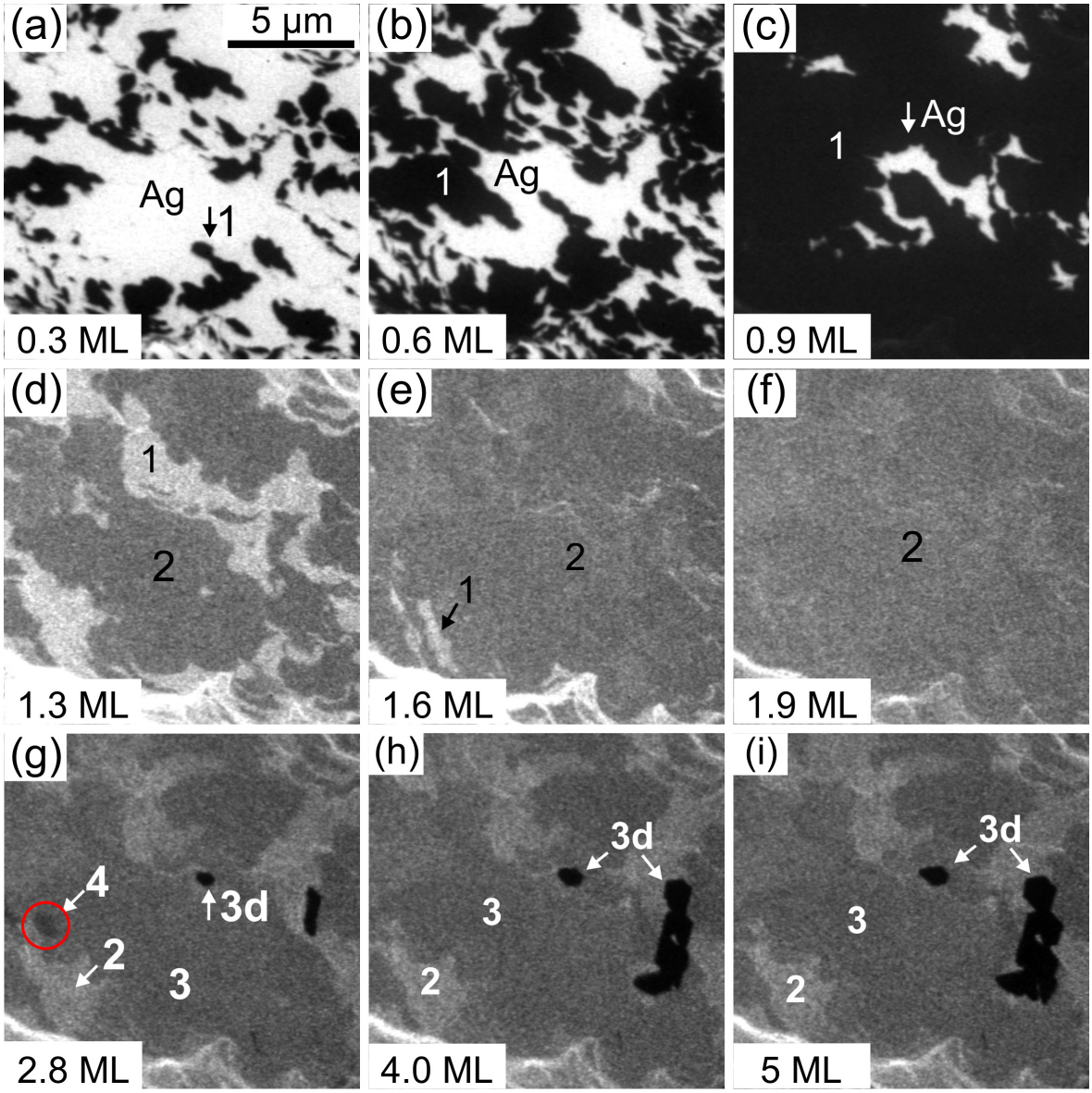

Figure 7.1: Growth of PTCDA/Ag(1 1 1) at 378 K: UV-PEEM images taken during growth. Deposition rate 0.2 ML/min. The labels Ag, 1 to 7, and 3D are meant to help the identification of the Ag substrate, the 1st to the 7th PTCDA layer, and the three-dimensional islands.

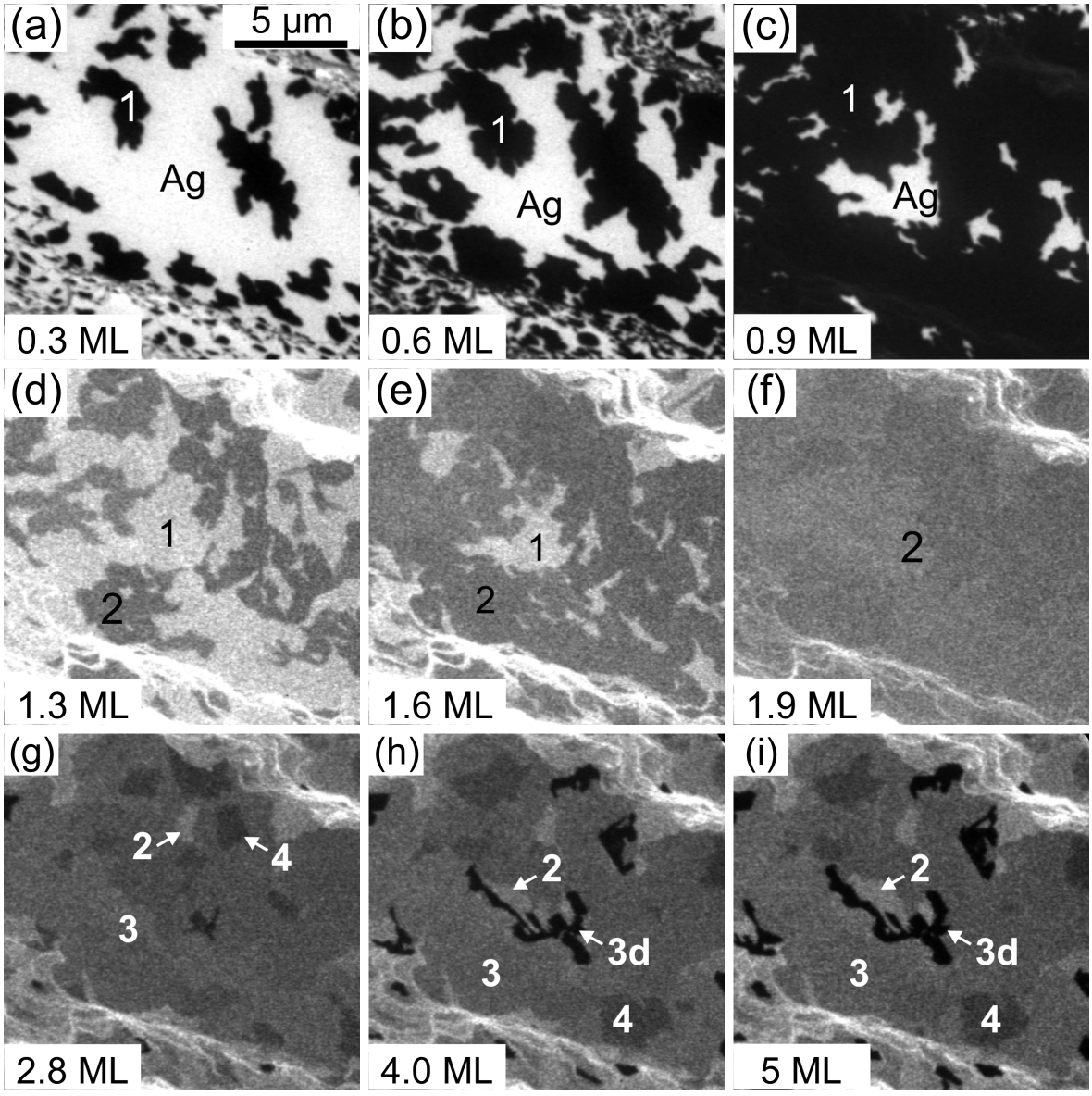

Figure 7.2: Growth of PTCDA/Ag(1 1 1) at 354 K: UV-PEEM images taken during growth.

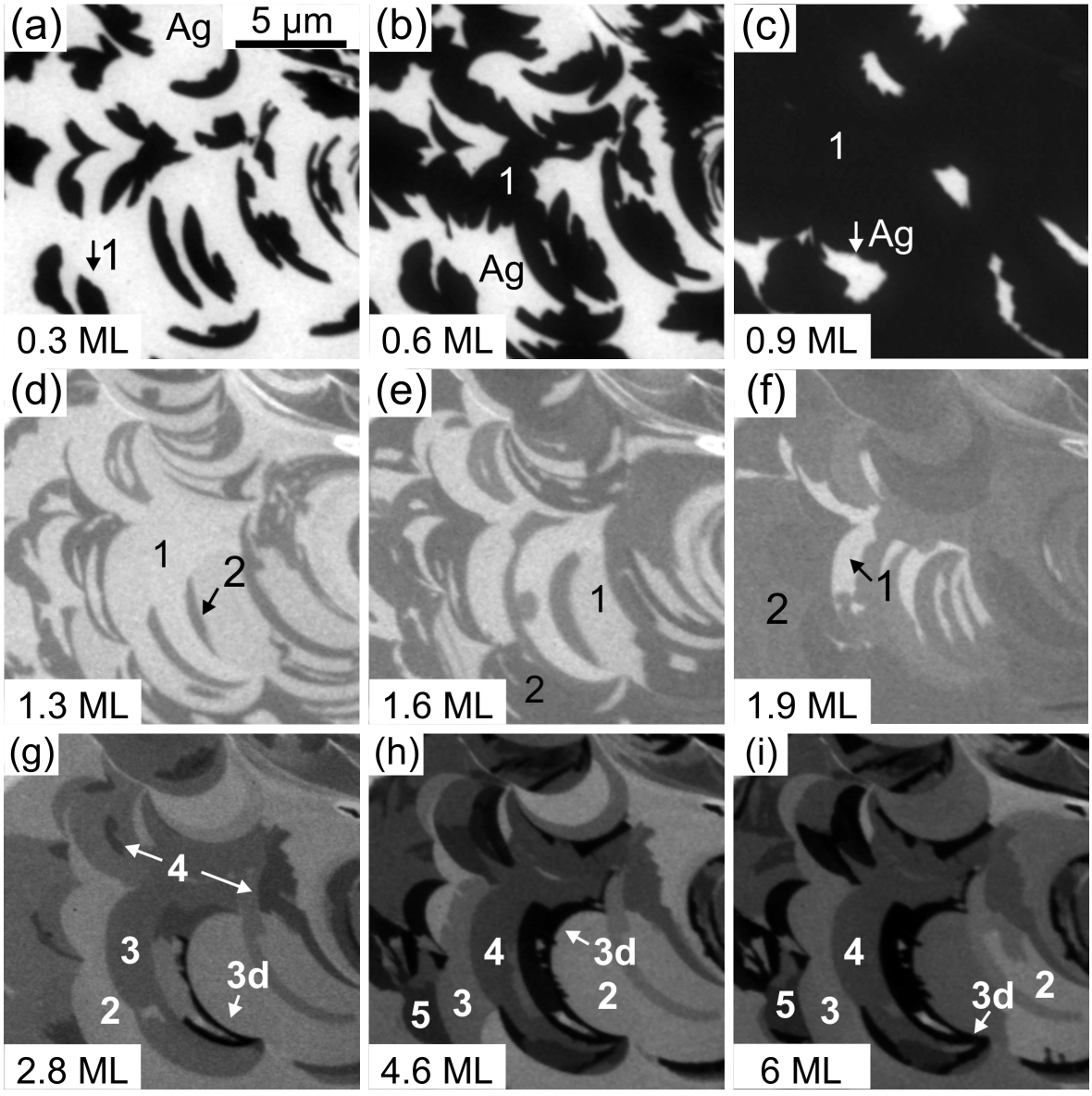

Figure 7.3: Growth of PTCDA/Ag(1 1 1) at 320 K: UV-PEEM images taken during growth.

always see a mixture of 3D islands and non-complete 3rd and higher layers. From the thermodynamical point of view this is remarkable, because only one species which is energetically favored should exist, either the 3D islands or the non-completed layers. However, this statement is only valid if the system is in thermodynamical equilibrium state what is clearly not the case during growth! As a consequence, energetically less favored phases are able to exist, but as we will see in the following, they are metastable and decay, if the growth kinetics allows a mass transport from the energetically less favored to the favored phases.

7.2 Decay of metastable islands

The decay of the fourth and third layer is shown in more detail in figure 7.4 (top and bottom row, respectively) for a substrate temperature of 378 K. At the end (Fig. 7.4.h) the (most likely) thermodynamically favored situation is reached: 3D islands on a completed bilayer. This situation can only be reached after a relatively long time and at reasonably elevated temperatures (but low enough to avoid desorption) without molecular flux. The reason is theat material transport is needed to transform the situation in Fig. 7.4.a into the "pure" Stranski-Krastanov situation. The transport is determined by the kinetics, mainly by the thermally driven diffusion and the molecular flux.

The topmost row of Fig. 7.4 shows the decay of the 4th layer during the growth. At this temperature desorption of the layer can be excluded by previous TDS-experiments [47] and of our own desorption experiments. The only explanation is therefore a mass transport from the 4th layer towards the growing 3D islands. The microscopic observation even allows to distinguish between two decay modes:

(i) direct and abrupt transformation from the 4th layer into a 3D island (see red circles in Fig. 7.4.a–b) and

(ii) the shrinking and complete disappearance of the 4th layer within 2.5 ML (see the two white circles in Fig. 7.4.d)

The areas of the fourth layer and the 3D island encircled in Figs. 7.4.a and 7.4b differ by a factor of 4. Due to the lack of material desorption, the height of the 3D

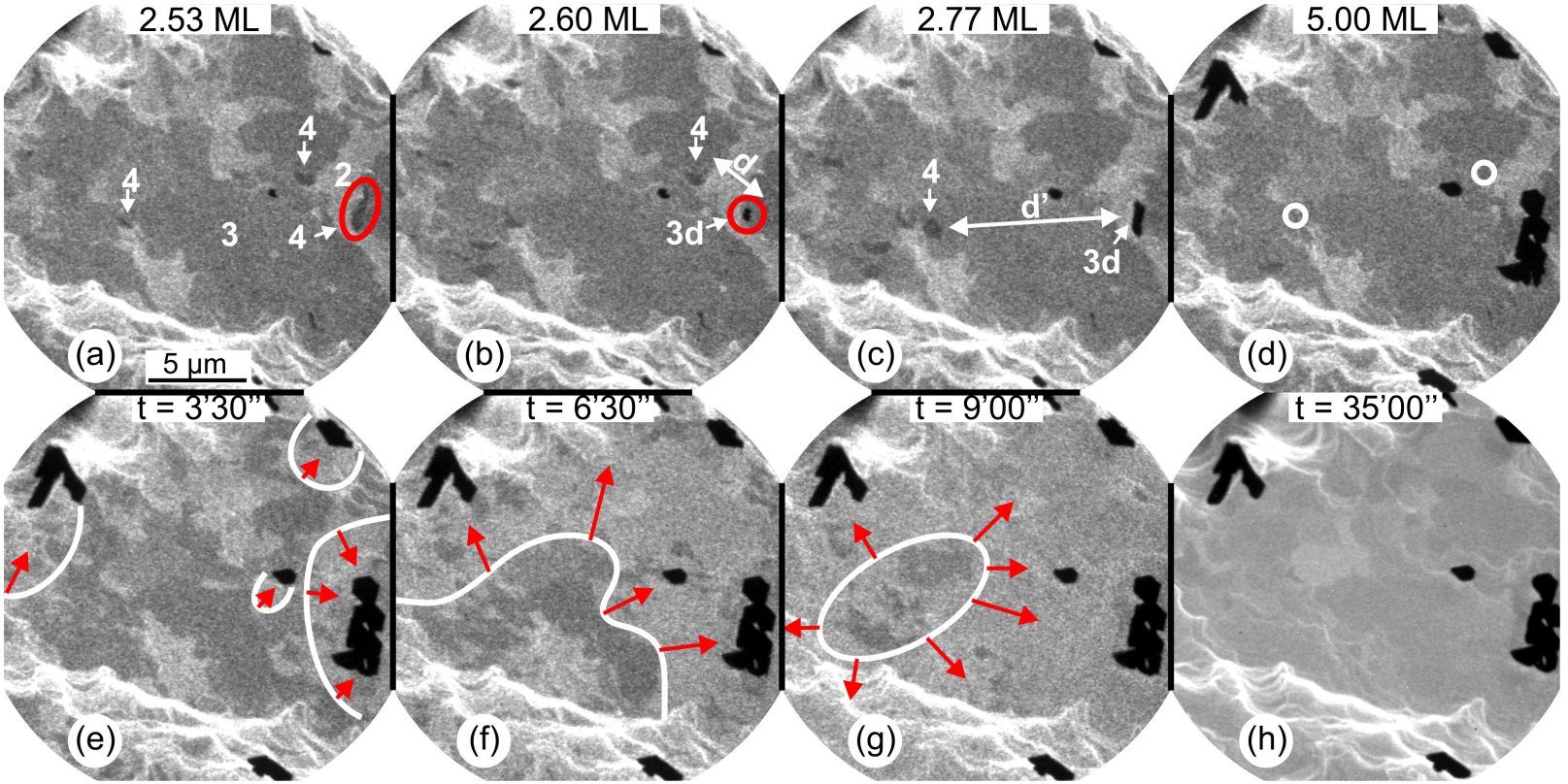

Figure 7.4: Decay of metastable islands. The figure shows details regarding metastabilities. In the first row the images have been taken during deposition at a substrate temperature of 378 K for the coverage indicated. In the second row the images have been taken at the same temperature, but after the deposition was finished. The time after the closure of the shutter is indicated in each image.

islands can be estimated as 4 layers above the 3rd layer, corresponding to 7 layers above the substrate surface. Even at a lower temperature of 354 K this transformation occurs between 2.8 ML and 4.0 ML (see the two 4th layer areas in the top center in Fig. 7.2.g transformed into two 3D islands in Fig. 7.2.h). Whereas at 378 K the 4th layer completely disappears at 5 ML (see Fig. 7.4d), the 4th layer islands at 354 K (still) exist, as long as the distance to a 3D island is greater than about 1 μm. At 320 K, the lowest temperature shown here, the 4th and even higher layers can co-exist in the direct neighborhood of 3D islands (see Figs. 7.3.h and 7.3.i).

In the temperature range up to 378 K the 3rd layer is clearly more stable than the 4th layer. At 378 K the amount of the 3rd layer does not change between 2.5 and 5.0 ML (see Fig. 7.4.a–d). The 3rd layer is stable even nearby the 3D islands (within an accuracy of approx. 100 nm). The situation changes drastically if the molecular flux is stopped: the 3rd layer decays within 35 min (see Fig. 7.4.e–h). The 3rd layer starts to disappear near the 3D islands. Around the 3D islands denuded zones are formed. These are marked by white lines in Fig. 7.4.e–g, which have been added as a guide for the eyes. The arrows represent the direction of an assumed material flux from the 3rd layer island to the 3D islands.

7.3 Kinetic description of metastable growth

A theoretical description of the growth kinetics is, e.g., given in the text book of *Pimpinelli and Villain* [85]. We will briefly review the well known description used for the atomic (or molecular) growth of stable phases. Finally, and that is our own approach, we will extend this description to cover also the growth of metastable islands near stable islands.

The combination of the material conservation law:

$$\frac{\partial}{\partial t} n(\vec{r}, t) = -\nabla \vec{j}(\vec{r}, t) \tag{7.1}$$

and the first Fick's law:

$$\vec{j}(\vec{r}, t) = -D \nabla n(\vec{r}, t) \tag{7.2}$$

yields the second Fick's law:

$$\frac{\partial}{\partial t} n(\vec{r},t) = D \triangle n(\vec{r},t) \tag{7.3}$$

where $n(\vec{r},t)$ is the density of free ad-atoms (or ad-molecules) at the time t and place $\vec{r}$. The gradient in the density causes a current $\vec{j}(\vec{r},t)$ which is determined by the diffusion constant D, which is assumed to be independent of $\vec{r}$.

This equation can be transferred to the situation of molecules diffusing on the surface after deposition with a flux F and that can desorb within a time constant τ_{des}:

$$\frac{\partial}{\partial t} n(\vec{r},t) = D \triangle n(\vec{r},t) - \frac{1}{\tau_{\mathrm{des}}} n(\vec{r},t) + F. \tag{7.4}$$

The equation describes the lattice gas density between two islands. In the situation of steady state, the lattice gas density n_{edge} near the edge of an island has a fixed value n_0, which corresponds to the "vapor pressure" at the interface of a liquid and a gas. If the density in front of the island edge is larger than n_0, then the island grows, otherwise it shrinks.

A known one-dimensional steady state solution of eq. (7.4) is:

$$n(x) = n_0 + \frac{F}{2D}\left(l^2 - x^2\right), \tag{7.5}$$

$$j(x) = F\,x \tag{7.6}$$

where any desorption is neglected. The coordinate x is measured from the center of the two islands, which are $2l$ apart from each other. The left column of figure 7.5 shows the density of the molecular gas and the molecular current between the two islands. During growth (i.e. $F \neq 0$) the gas density has a parabolic shape with a maximum in the center (i.e. $x = 0$), resulting in a symmetric portion of molecular flux towards the left ($j < 0$) and the right ($j > 0$). The molecular current at the edge of the islands is on both sides:

$$j_0 = j(x = \pm l) = \pm F\,l \tag{7.7}$$

and is independent of the diffusion constant D! As soon as the molecular flux is interrupted ($F = 0$), the molecular current becomes $j(x) = 0$ and the density of the

molecular gas is constant: $n(x) = n_0$. This is the situation of thermodynamical equilibrium, for which we would not observe changes, when, e.g., the growth is interrupted.

Based on this, we start a new approach to describe our observations of island metastability. Therefore we introduce the new parameter $n_{3\mathrm{d}}$, which represents the equilibrium molecular density near the edge of a 3D island. Because the 3D islands are energetically favored, the value of $n_{3\mathrm{d}}$ is clearly smaller than n_0. With the new boundary condition we obtain from eq. (7.4):

$$n(x) = \frac{n_0 + n_{3\mathrm{d}}}{2} + \frac{F}{2D}\left(l^2 + \Delta x^2 - (x - \Delta x)^2\right), \tag{7.8}$$

$$j(x) = F\,(x - \Delta x) \tag{7.9}$$

with $\Delta x = -\frac{D}{2Fl}\,(n_0 - n_{3D})$ which represents the position of the maximum in the gas density $n(x)$ — relative to the center between the two islands. As Fig. 7.5 shows on the right side, the maximum of the parabolic molecular density curve shifts from the center towards the 2D-island, if the molecular flux F is lowered. At a certain flux (here at F_0) the maximum can even be at the edge of the 2D island. This is the case when the island cannot grow any more, which is also seen in the behavior of the molecular current (bottom of the right column in Fig. 7.5). The currents at the edges of the 2D islands and of the 3D islands are:

$$j_{2\mathrm{d}} = -F\,l + \frac{D}{2l}\,(n_0 - n_{3\mathrm{d}}), \tag{7.10}$$

$$j_{3\mathrm{d}} = F\,l + \frac{D}{2l}\,(n_0 - n_{3\mathrm{d}}). \tag{7.11}$$

The first part of this formula depends on the flux F and represents the contribution already discussed for eq. (7.7), the second part depends on the different molecular densities n_0 and $n_{3\mathrm{d}}$ at the 2D and 3D island edge, respectively. This density difference leads to a diffusion current from the 2D to the 3D island. If the molecular flux is stopped ($F = 0$) then this contribution of the current still exists. It leads to a shrinking of the 2D island and a growth of the 3D island ($j > 0$ means mass transport to the right). The velocity of the mass transport is determined by the diffusion and is therefore temperature dependent.

Besides this flux (i.e. deposition rate) dependence, the current $j_{2\mathrm{d}}$ is influenced by the distance $L = 2l$ between the 2D and the 3D island. There is a critical distance $\tilde{L}$

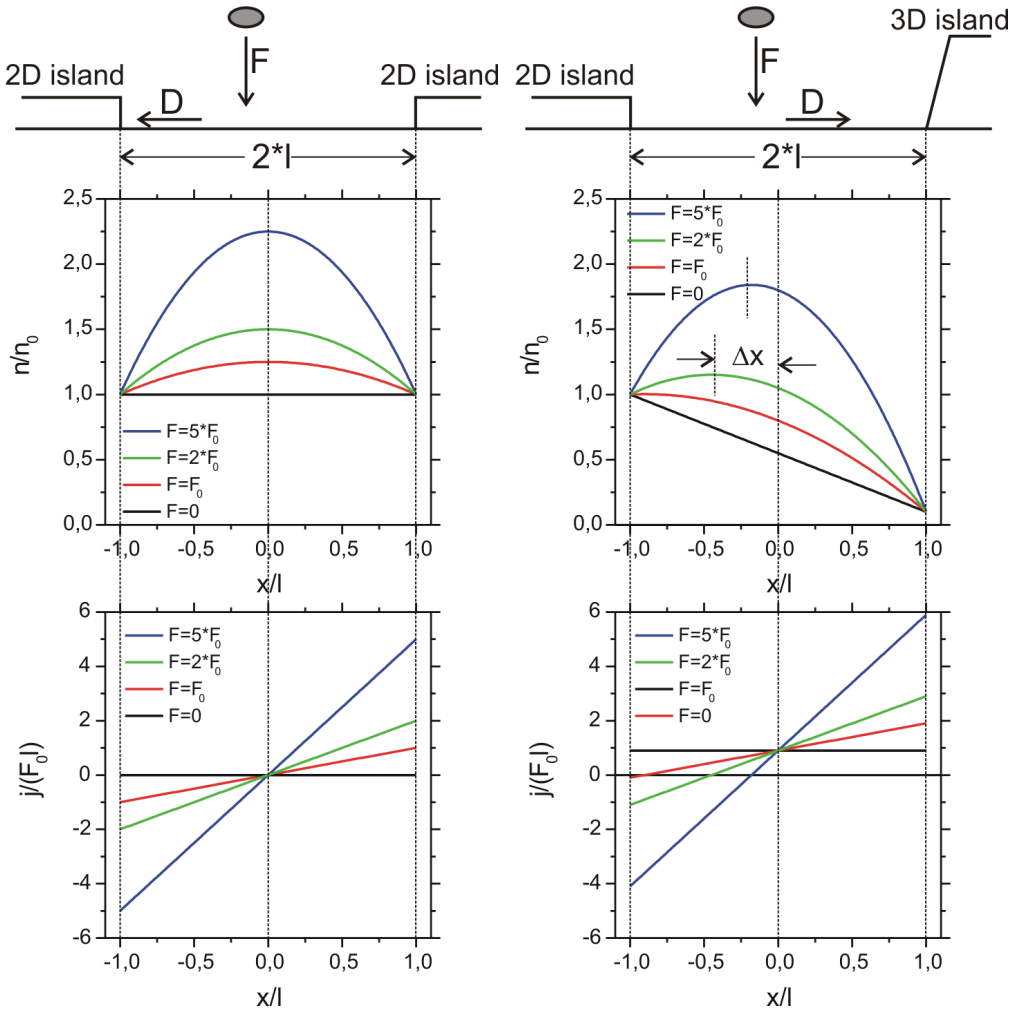

Figure 7.5: Interplay of flux and kinetically driven stability. The graphs show solutions of eq. 7.5 and eq. 7.8 for four different flux values for an area between two 2D islands on the left side and between a 2D and a 3D island on the right. The chosen parameters D, F_0, l and n_0 are scaled in the way, that $\frac{F_0}{2D}l^2 = \frac{n_0}{4}$. The value n_{3d} is set to $n_{3d} = n_0/10$.

determining whether the 2D island can grow or shrink:

$$\tilde{L} = \sqrt{2\,\frac{D}{F}\,(n_0 - n_{3\mathrm{d}})}. \tag{7.12}$$

For any 2D island inside this distance to the 3D island, the current $j_{2\mathrm{d}} > 0$ corresponds to a mass transport to the 3D island. At greater distances the 2D islands can grow in size until the distance is shrunk to $L = \tilde{L}$. As a consequence a denuded zone is formed around the 3D islands.

The temperature dependence is given by an Arrhenius-like behavior of D, n_0 and $n_{3\mathrm{d}}$:

$$\begin{aligned}\tilde{L} &= \sqrt{2\,\frac{D_0}{F}}\exp\left(-\frac{E_{\mathrm{d}}}{kT}\right)^{1/2} \quad \sqrt{\exp\left(-\frac{E_{\mathrm{step2d}}}{kT}\right) - \exp\left(-\frac{E_{\mathrm{step3d}}}{kT}\right)} \\ &= \sqrt{2\,\frac{D_0}{F}}\exp\left(-\frac{E_{\mathrm{d}} + E_{\mathrm{step2d}}}{kT}\right)^{1/2} \quad \sqrt{1 - \exp\left(-\frac{E_{\mathrm{step3d}} - E_{\mathrm{step2d}}}{kT}\right)},\end{aligned} \tag{7.13}$$

where E_{d} is the activation energy of surface diffusion , D_0 the pre-exponential factor (in the order of $10^{-13}\mathrm{sec}^{-1}$), E_{step2d} and E_{step3d} are the binding energies of a molecule at the 2D step edge and at the 3D island, respectively. The diffusion energy is in the order of about 50 to 100 meV, whereas the binding energies are clearly higher (in the order of a few 100 meV). The size of the denuded zone, where no metastable island can exist, shrinks with temperature by a *quasi* Arrhenius-like behavior. A simple estimation whether the 2D islands can co-exist or completely shrink is the relation between the size of the denuded zone $\tilde{L}$ and the average distance $L_{3\mathrm{D}}$ between two 3D islands.

$$\tilde{L} \;<\; \frac{L_{3\mathrm{D}}}{2} \qquad \Rightarrow \qquad \text{2D island grows} \tag{7.14}$$

$$\tilde{L} \;>\; \frac{L_{3\mathrm{D}}}{2} \qquad \Rightarrow \qquad \text{2D island shrinks} \tag{7.15}$$

The previous relations can be used to predict the growth mode. To do so, we attempt a rough estimation of $\tilde{L}$ for the third layer. The average size of the denuded region is related to the island density by $n_x = \frac{1}{\tilde{L}^2}$. Since we have not calculated the island density for the 3$^{\mathrm{rd}}$ and 4$^{\mathrm{th}}$ layer, and we assume them to be equal to that of the second layer. Furthermore, for a large island the energy of adsorption of a molecule is (see equation (6.2)) $E_i/i = E_{\mathrm{step2d}}$. The values of E_i are found in table 6.1.

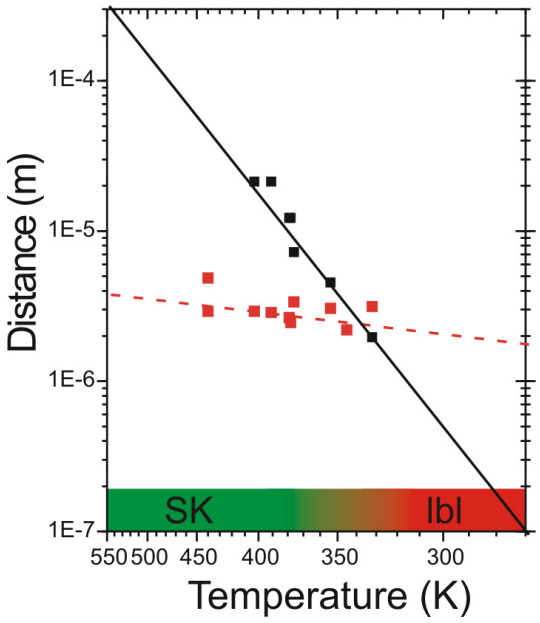

Figure 7.6: The distances of 3D islands (black straight line) and the 2nd layer nucleation centers (red dashed line). Data are taken from Fig. (5.3) for the flat area. In the bottom the regimes for Stranski-Krastonov and layer by layer growth are indicated.

The results are plotted in figure 7.6. The lower bar marks the transition as observed from the experiments. The calculated result is in disagreement with the observed transition. Apparently the growth mode transition is not a consequence of the presence of the metastable layers. Other parameters such as a thermodynamic different stability of the α- and β-PTCDA crystal structure could play a significant role and actually regulate the growth mode.

Up to now we have discussed and tried to explain by a kinematic description what happens when the metastable 4^{th} and 3^{rd} layer islands co-exist with 3D islands. The important question is why the 3^{rd} and 4^{th} layer islands are nucleated, though they are energetically less favored compared to the 3D islands. It is even the experimental observation that in the investigated temperature range of 300 K to 400 K the metastable 3^{rd} layer is always formed before the stable 3D islands grow. The 4^{th} layer islands are created at the same time as the 3D islands. The reason, why the energetically unfavored islands are formed, before or at the same time, as the 3D islands is found in the nucleation process. Following the approach by *Venables* [72] the nucleation occurs in

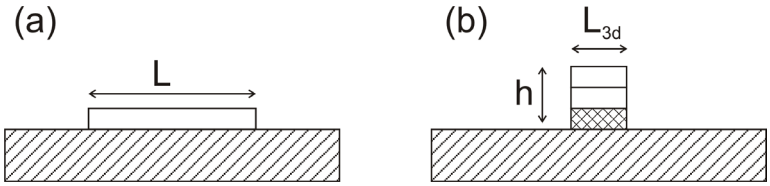

Figure 7.7: Model for cluster stability.

the following steps: first the density of diffusing ad-molecules increases under deposition until a saturation density is reached. Clusters of molecules are then formed that can either continue growing by attachment of further molecules (and therefore acts as nuclei for the growth) or they can shrink and decay. The stability of a cluster depends on its cluster size i. The largest unstable cluster is the so-called *critical cluster* of size i^*. The simplest assumption is $i^* = 1$, that means the smallest stable cluster consists of two molecules. A further point is the shape of this cluster, especially for larger cluster sizes. For example, a long chain of molecules does not have the same stability as a compact round cluster. This is mainly due to the energy gain by intermolecular bonding. A further point, which is not deeply discussed in the literature, is the dimensionality of the cluster: one-, two- or three-dimensional. Furthermore clusters can diffuse, and only the agglomeration of many clusters forms a nucleus for growth.

In our case we have to compare the start of the two-dimensional island growth of the 3^{rd} (and 4^{th}) layer with that of the three-dimensional islands. As discussed above there are two possibilities to form a 3D island: (i) by nucleation on a free terrace involving the formation of a 3D cluster and (ii) a transformation of a 4th layer into a 3D island. The latter case is observed for about every third 3D island at temperatures above 350 K. The first case is the classical way of nucleation by forming isolated clusters. There must be an essential difference between the two nucleus clusters for the 2D and 3D island, otherwise it would be not determined whether the growth should be strictly two-dimensional or three-dimensional. Some of these differences observed, e.g. by TEM for Ge/Si(1 1 1) [86], are dislocations at the interface which compensate for the strain due to lattice mismatch. The formation of a dislocation network is energetically unfavored, but the subsequent layers grow without strain, thus gaining energy. An energy balance between (a) the energy loss due to dislocation formation and (b) the energy gain due to growth without strain decides whether a three dimensional cluster is stable.

Fig. 7.7 compares a 2D and a 3D island (or cluster). The volume of the two islands should be the same, i.e. $L = L_{3D} \cdot h$ with L being the number of molecules in the 2D island, , L_{3D} those in one layer of the 3D island and h the number of molecular layers.

When a molecule attaches to the 2D island the system will gain an energy ΔE_{2D}, which includes also the energy loss due to the strain by lattice mismatch. ΔE_{3D} is the gain in energy when a molecule attaches on top of the 3D island which is free of strain. We assume that this gain in energy is the same for all levels in the 3D islands, except for the interface layer, where dislocations have to be created. Here the energy gain is reduced by $\Delta E_{\text{dislocation}}$, yielding in an interface energy gain of $\Delta E_{3D} - \Delta E_{\text{dislocation}}$.

For the 2D island the overall energy gain is:

$$E_{2D} = L\,\Delta E_{2D} \tag{7.16}$$

and for the 3D island:

$$\begin{aligned} E_{3D} &= L_{3D}\,((\Delta E_{3D} - \Delta E_{\text{dislocation}}) + (h-1)\,\Delta E_{3D}) \\ &= L_{3D}\,h\left(\Delta E_{3D} - \frac{\Delta E_{\text{dislocation}}}{h}\right) \\ &= L\left(\Delta E_{3D} - \frac{\Delta E_{\text{dislocation}}}{h}\right) \end{aligned} \tag{7.17}$$

The following energy balance decides whether an 2D or a 3D island is energetically favored:

$$\Delta E = E_{3D} - E_{2D} \;>\; 0 \;\Rightarrow\; 3D\ islands; favored \tag{7.18}$$

$$<\; 0 \;\Rightarrow\; 2D\ islands; favored \tag{7.19}$$

We assume, that it is more favorable for a molecule to attach on top of a 3D island than at a 2D island (i.e. $\Delta E_{3D} > \Delta E_{2D}$). Then, from the eq. (7.16) and (7.17) a critical island height h^* can be calculated assuming equal lateral sizes, for which the energy gain of the topmost layer compensates for the loss at the interface:

$$h^* = \frac{E_{\text{dislocation}}}{\Delta E_{3D} - \Delta E_{2D}}. \tag{7.20}$$

For all 3D island higher than this critical height $h > h^*$, the 3D island is energetically stabilized.

In this model we assume dislocations at the interface between the 3D island and the substrate, compensating for the strain due to lattice stress. This model can also be extended to further types of compensating interface layers (e.g. change in molecular orientation, electronic states and changes in crystal structure of the 3D islands from the α- to the β-morphology). This interface layer has to be built by the energy cost compared to a 2D island. The gain in energy in the following layer will compensate this lost.

With this simple view it is clear, that a 3D cluster needs to have a certain height in order to be stable. This three dimensional rearrangement reduces significantly the formation probability compared to the 2D cluster, which is "simply" formed by an in-plane agglomeration of molecules. Therefore the 3D islands are not nucleating first, though they are energetically favored. From the observed transformation of the 4^{th} layer islands to 3D islands the critical height h^* can be experimentally estimated as about 4 layers above the 3rd layer interface (or 5 layers above the stable 3^{rd} layer). The fact, that the 3D islands have a lower nucleation probability, can be seen indirectly in our experiments: the 3D islands are mostly nucleating at a step bunch or in areas with high step density. The step bunch acts here most likely as a nucleation center to stabilize the strain in the small 3D cluster.

7.4 Discussion and conclusion

We microscopically observed the growth mode transition from a quasi layer-by-layer at low temperatures to Stranski-Krastanov. During the growth, we observe two types of decay of metastable layers. In one case a 2D island is converted abruptly to a 3D island and in the other case two 2D islands progressively disappear. Two theoretical explanations are given to explain the metastability.

In a one dimensional description of the growth between two species with the same thermodynamical stability, represented by n_0, the dependance of the molecular density and the molecular flux are described by equations (7.5) and (7.6). Upon introduction of a thermodynamic asymmetry the system is destabilized and the region with the highest molecular density is shifted towards the less-stable (metastable) layer. In these conditions, the most stable species is also the one receiving the highest net flux of

molecules. However, both species can grow, but at different rates. At a critical distance $\tilde{L}$, which depends on the intrinsic thermodynamic stability of the 2D and 3D islands and on the flux, the 2D islands do not grow anymore, or in other words are stabilized. Upon perturbation of the system, e.g. by decrease of the flux, the 2D islands disappear as shown in figure 7.4.

We have related the second case, of abrupt transition of a 2D-island to a 3D-island, to the formation of an energetically un-favored interface. The *vertical* transition compensates for the interface energy.

The growth observed, is not typically observed in standard atomic growth. One reason for this might be that in organic growth very often polymorphism occurs, i.e. several of possible crystal structures, island shapes, orientations, etc. exist, which have only small energy differences. Due to the molecular geometry, more arrangements are possible compared to the atoms which are treated as isotropic. Therefore entropy plays a more important role.

Furthermore, also the nucleation and diffusion processes might be different. We have used the simple view of atomic nucleation and diffusion processes - commonly used for metallic atoms, which are typically treated as isotropic spheres.

In our case, the organic molecules are non-isotropic, have functional groups, and cover more than one substrate unit cell. The diffusion of molecules on the surface most likely occurs with a migration with the perylene backbone parallel to the surface. The formation of a cluster has different formation probabilities than isotropic spheres: the molecules need to rearrange in a way, so that the functional group interaction is optimized.