Self-Limited Growth in Pentacene Thin Films

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ABSTRACT: Pentacene is one of the most studied organic semiconducting materials. While many aspects of the film formation have already been identified in very thin films, this study provides new insight into the transition from the metastable thin-film phase to bulk phase polymorphs. This study focuses on the growth behavior of pentacene within thin films as a function of film thickness ranging from 20 to 300 nm. By employing various X-ray diffraction methods, combined with supporting atomic force microscopy investigations, one crystalline orientation for the thin-film phase is observed, while three differently tilted bulk phase orientations are found. First, bulk phase crystallites grow with their 00L planes parallel to the substrate surface; second, however, crystallites tilted by 0.75° with respect to the substrate are found, which clearly dominate the former in ratio; third, a different bulk phase polymorph with crystallites tilted by 21° is found. The transition from the thin-film phase to the bulk phase is rationalized by the nucleation of the latter at the thin-film-phase crystallites. This leads to a self-limiting growth of the thin-film phase and explains the thickness-dependent phase behavior observed in pentacene thin films, showing that a large amount of material is present in the bulk phase much earlier during the film growth than previously thought.

KEYWORDS: pentacene, polymorphism, organic thin film growth, organic semiconductors, X-ray diffraction, thin film morphology

INTRODUCTION

Pentacene is a prototypical organic semiconductor material for use in organic thin-film transistors.1−4 Well-defined deposition conditions under (ultra)high-vacuum conditions allow for a high reproducibility in thin-film fabrication, which also makes it an ideal model molecule for studying nucleation and crystal growth of conjugated organic molecules on surfaces in general.5−7 Pentacene is reported to grow in various different polymorphs, among which three distinct crystallographic phases have been observed on silicon oxide.8−10 During initial film growth, a monolayer of vertically upright-standing molecules forms directly at the organic−substrate interface.11 Thereafter, the so-called thin-film phase starts to develop, consisting of crystals built by molecules standing slightly inclined by about 3° relative to the surface normal.12 Further growth is characterized by rapid roughening due to three-dimensional island formation.13,14

In the vicinity of the thin-film phase, the so-called Campbell phase15 is reported to grow simultaneously.16 In this bulk phase polymorph, pentacene molecules exhibit an even higher inclination angle with respect to the substrate normal. From numerous studies, it is well established that the thin-film phase is only able to form close to the substrate interface. In fact, an approximate maximum of 50 nm (≈30 monolayers)10 is typically found to arrange in the thin-film phase, after which the film growth is dominated by the Campbell phase instead. The reason for this transition in growth behavior is still not fully understood, although many studies demonstrate how the extension of the thin-film phase can be manipulated by employing different substrate treatments, deposition conditions (e.g., deposition rate, glancing-angle deposition, temperature, pressure, etc.),17 or by codeposition with chemically modified pentacene species, where phase separation promotes growth in the thin-film phase.18,19 The metastable thin-film phase can be transformed into the Campbell phase by either heat treatment, solvent treatment, or aging, which is evident from experimental studies and molecular dynamics calculations.20−23 Moreover, some recent results show that Campbell phase crystallites not only grow with their 001 contact plane parallel to the thin film polymorph, but additionally with their 001 contact plane inclined by well-defined angles of 5°, 10°, or 13°.24−26 While homoepitaxy between the 001TF (thin film) and 001C (Campbell) planes might appear obvious, the appearance of

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inclined structures on the terraced 3D islands is surprising, and the mechanisms behind their formation remain unresolved. Polymorphism in thin films is of great importance as it can have a profound effect on various physical properties. This is certainly true for pentacene, where charge transport behavior is clearly different in the respective polymorphs. In cases where a material with multiple polymorphs is to be used in an organic electronic device, it is preferable to have phase pure films. A material with multiple polymorphs is to be used in an organic electronic device, it is preferable to have phase pure films in order to reduce charge trapping at the grain boundaries formed between the different phases. Such an effect has been observed in pentacene thin films, whereby phase pure films show superior charge transport properties compared with mixed phase films. Having a deeper understanding of the growth mechanism and phase transition behavior may allow simpler routes to phase pure films to be developed and improved devices to be produced from polymeric materials in general.

By evaluating a number of pentacene thin films of distinct layer thickness by atomic force microscopy and X-ray diffraction experiments, the focus here is on detecting various defined bulk phase crystallite orientations, which can be related to the respective growth stages/thicknesses of the thin-film phase. Such a determination allows the molecular arrangements of bulk phase molecules with respect to the underlying thin-film phase to be determined. Finally, a potential explanation for the formation of the bulk phase within the thin films is given, which is derived by combining new experimental results with previous observations on thickness-dependent defect formation.

## EXPERIMENTAL SECTION

Pentacene was purchased from Sigma-Aldrich and used without further purification. Pentacene films were grown via physical vapor deposition at a pressure of $<5 \times 10^{-6}$ mbar. 1 × 1 cm sized silicon wafers with a thermally grown silicon oxide layer of 150 nm were used as substrates. The substrates were solvent-cleaned in acetone using ultrasonication for 10 min, rinsed afterward with isopropanol, and dried under a nitrogen stream. Additional cleaning was performed under vacuum conditions: substrates have been Ar$^+$ ion sputtered for 10 min at a pressure of ca. 5 × 10$^{-5}$ mbar using a 1 keV acceleration voltage and a current of 30 mA. Pentacene layers with various thicknesses ranging between 20 and 300 nm were prepared. Substrates were kept at ambient temperature during deposition, and a growth rate of ca. 0.5 nm/min was used, as monitored by a quartz crystal microbalance. In addition, samples of 50 and 180 nm nominal thickness were prepared under slightly different conditions which are described elsewhere.

Specular X-ray reflectivity/diffraction measurements were performed on a PANalytical Empyrean diffractometer equipped with a copper sealed tube, a multilayer mirror forming a monochromatic beam (wavelength $\lambda = 0.154$ nm), and divergence slits on the primary side. On the secondary side, a receiving slit and 0.02 rad Soller slit were used. A PANalytical PIXcel 3D detector in point detector mode collected the scattered intensity. For the sake of comparability, the angular measurements ($2\theta$) are transformed to a reciprocal space representation via $q_z = (4\pi/\lambda) \sin \theta$, with $q_z$ being the scattering vector perpendicular to the substrate. For the X-ray pattern simulations the X’pert Reflectivity software (PANalytical) was used, which employs the Parratt formalism. To acquire additional information on the film mosaicity and possible inclinations of crystallites, rocking curve measurements were performed using the same setup. In such a scan, the length of the scattering vector is kept constant, and the sample is rotated/rocked allowing access to netplanes in directions other than the specular (i.e., parallel to the substrate surface).

Grazing incidence X-ray diffraction (GIXD) measurements were performed on beamline ID10 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. An X-ray energy of 22 keV and a beam size of 20 × 20 μm were used. The sample was mounted on a moveable stage so that a defined incidence angle, $\alpha$, could be set to 0.06°. This is slightly below the critical angle of total external reflection, $\alpha_c$, of the substrate in order to suppress signal from the amorphous SiO$_2$. A PILATUS 1M detector was mounted on a two-way movable detector arm allowing a large angular/reciprocal space region to be investigated. The collected data were converted to a reciprocal space representation using the xrayutilities library and further analyzed using the software PyGID. The data are represented as two-dimensional contour plots with a linear scaled color code ranging from blue (low intensity) to red (high intensity).

Atomic force microscopy (AFM) measurements have been performed on a Nanosurf Easyscan 2 with a 70 μm scan head in tapping mode, equipped with silicon-spm-sensor tips of type PPP-NCLR. Data were analyzed using the software Gwyddion.

## RESULTS

### X-ray Diffraction

Specular X-ray diffraction patterns from samples of different nominal pentacene thicknesses are depicted in Figure 1. The curves for all samples show an increase in intensity at low angles, which represents the area of total external reflection and reducing footprint as the scattering angle (vector) increases. At about 0.03 Å$^{-1}$ the intensity starts to decrease, typical for X-rays starting to penetrate the substrate surface. In the curve of the 20 nm sample, there are two distinct features superimposed. First, Kiessig fringes of two different periodicities occur, meaning that there are at least two types of layers in this system. Higher periodic Kiessig fringes (hardly noticeable in this image representation) correspond to the 150 nm silicon dioxide layer of the substrate. Fringes of lower periodicity have been fitted to a layer thickness of 12 nm. Such pronounced oscillations only occur if a well-defined, flat, and homogeneous pentacene layer exists. It can be assigned to the first layers of the pentacene adsorbate located directly at the substrate surface. The second set of features present is Bragg peaks at 0.407 and 0.814 Å$^{-1}$, corresponding to d-spacings of 15.44 and 7.72 Å, respectively. Comparison with literature data shows that these are the 001 and 002 peaks of the pentacene thin-film phase. With a low nominal thickness of 20 nm, these peaks exhibit a small shift to lower $q_z$ values, which is due to a layer-thickness-dependent interference between the beam diffracted by the pentacene crystallites and the optical reflectivity from the substrate. The pattern shows peaks belonging to the 00L series, this further means that...
the crystallites are formed by upright-standing molecules, with the 001 plane parallel to the substrate surface. For the thicker film of 100 nm, the behavior is similar, with the Kiessig fringes below 0.3 Å⁻¹ being essentially the same as in the 20 nm sample. Concerning the Bragg peaks, the peaks at 0.407 and 0.814 Å⁻¹ are more intense and of significantly smaller width. According to the Scherrer formalism, the film containing more pentacene has developed crystals with a much larger vertical extension, or in other words, the initial crystals grow into larger crystals rather than forming new grains, which agrees well with an earlier report.

For the 100 nm film, additional Bragg peaks occur at \( q_x = 0.433 \) and 0.866 Å⁻¹ (Figure 1, red curve). These peaks correspond to the 00L peak series of the Campbell phase, bulk polymorph, with the peak series reflecting a \( d_{001} = 14.50 \) Å spacing (dotted lines in Figure 1). Compared to the previous samples, the sample with a nominal thickness of 300 nm shows, again, more intense and sharper Bragg peaks. Despite the bulk phase beginning to grow, the thin-film phase still continues to grow, at least up to a nominal film thickness of 300 nm.

The specular diffraction patterns presented in Figure 1 only provide information on the crystal netplanes that are parallel to the substrate surface. As such, there is no information on the degree of crystal alignment (mosaicty), i.e., if some of these netplanes also develop with an inclination to the surface. To gather this information, rocking curves were recorded on the 001 peaks of both the thin-film and Campbell phase and compared; the data are depicted in Figure 2. Starting with the thin-film phase peaks, a very similar behavior is observed independent of the layer thickness (Figure 2A): a strong specular peak at \( \Delta \omega = 0^\circ \) with a narrow fwhm of about 0.1° is observed. The maximum intensity of these curves increases with the layer thickness. Additionally to the sharp peak, a broad diffuse contribution is present, which is commonly assigned to dislocations being present in the films.

Identical measurements performed on the 001 reflection from the Campbell phase reveal a markedly different scenario (Figure 2B). First, a dominating specular peak occurs (\( \Delta \omega = 0^\circ \)) with a fwhm of about 0.25°. This width is significantly larger as compared to the sharp contribution of the thin-film phase. This indicates that the order with respect to the substrate surface is less defined, or in other words, the mosaicity is much larger than the mosaicity of the thin-film phase crystallites.

Besides these central peaks, the rocking curves clearly show the presence of additional satellite peaks with their maximums being inclined by 0.75° to the specular direction. This means that there is another crystal orientation of the bulk phase, either due to the substrate or due to the underlying film, which causes the 001 planes to grow inclined by 0.75°. Compared to the specular peaks, these satellite peaks possess a much larger width, meaning that this inclined crystal species has more freedom to adjust itself. Notably, these 0.75° inclined features are also common to the 002, peak and higher order reflections (00L, data not shown), which demonstrates that this feature is a result of mosaicity rather than a geometrical effect like overlap of the thin-film phase peaks with the Campbell phase peaks. Importantly, the very same satellites are present in pentacene samples of different nominal thicknesses, meaning that these inclined crystallites develop in films as thin as 50 nm.

**Grazing Incidence X-ray Diffraction.** The specular and rocking curve measurements provide information on the netplanes essentially parallel to the substrate surface. To access additional reciprocal space volumes, GIXD measurements were performed on various samples, and the respective reciprocal space maps are provided in Figure 3. These measurements allow information about the in-plane structure to be observed, as peaks now also have a contribution from the in-plane scattering vector, \( q_{xy} \), as well as from the out-of-plane scattering vector, \( q_z \). The map in Figure 3A shows the results of a 20 nm sample and shows a large number of peaks distributed over the investigated area of reciprocal space. Starting with the area close to \( q_z = 0 \) Å⁻¹, there is a peak located at around \( q_x = 0.41 \) Å⁻¹ which belongs to the 001 reflection of the thin-film phase and corresponds to that known already from the specular scans and rocking curves. Because of geometry constraints, specular information is not fully accessible in a GIXD map (area of constant blue color at low \( q_z \)). As the thin-film phase peak has a relatively high intensity, one observes the tails of the specular peaks smearing into the detectable area along Debye–Scherrer rings due to crystallite mosaicity.

At large \( q_{xy} \) values (>1 Å⁻¹), there are multiple peaks which lie along \( q_x \) at a constant \( q_{xy} \). A comparison with calculated peak positions on the basis of the known crystal structures reveals that all of these peaks result from the thin-film phase. A 001 contact plane of the thin-film phase crystals is sufficient to explain all peaks, and this agrees well with previous findings.

Performing the same GIXD measurements on the 100 nm sample (Figure 3B) results, however, in a different pattern, which contains, in addition to the peaks already found in the 20 nm sample, various new features. These are the result of pentacene starting to develop bulk phase crystals in the Campbell phase with a 001 contact plane. This is obvious also from peaks close to the specular direction in GIXD (\( q_{xy} = 0 \).
intense peaks of this new phase are located at small $q_{\parallel}$ values (indexed as the 00$L$ series in Figure 3C). These peaks align along a common line through the origin ($q_{\parallel} = q_{\perp} = 0 \text{ Å}^{-1}$) but with an angle of 21° with respect to the specular direction. Note that these peaks are only detectable in the GIXD maps, as the tilt of 21° is beyond the geometrical limits of a conventional rocking curve measurement performed at small scattering vectors. At larger $q_{\parallel}$ values, three additional peaks appear (indexed as the $-1-1L$ series in Figure 3C). The presence of these peaks clearly indicates that a second pentacene bulk phase polymorph now appears in the film, that is, the so-called Holmes bulk phase.41 As this species appears only in the data for the 300 nm thick films, it can be concluded that it develops at a later stage in the growth process. Overall, the X-ray diffraction analysis provides evidence for the presence of an additional bulk phase species in the Holmes phase that lies with the 001 plane at a well-defined tilt angle of 21° from the surface normal.

**Atomic Force Microscopy.** For the investigation of the surface topography, AFM height scan measurements have been performed; representative AFM micrographs of the various samples are depicted in Figure 4. Starting with the sample of 20 nm nominal thickness (cf. Figure 4A), this shows clear three-dimensional island structures. Similar to the case of a pentacene monolayer,42 these structures are of dendritic shape. Furthermore, the terraces are preserved, resulting in a steplike increase of the structure height in the image, as frequently reported for pentacene thin films.43,44 The step height is in the range of 14−16 Å, as expected for pentacene grown with a 00$L$ orientation, which means each step corresponds to a single pentacene layer. Note that polymorph determination from the step height lies beyond the resolution of the AFM setup. The roughness, $\sigma_{\text{RMS}}$, of the film is determined to be 2.5 nm, and the incline distribution shows a maximum at a slope angle of 0.3° (cf. Figure 4D, red line). A closer look at a pentacene island in the 20 nm film reveals that the dendritic branches grow nearly independently to adjacent ones. Although the terrace height seems to be constant throughout different branches, cracks are formed and adjacent branches, even within one island, do not coalesce.

Upon further pentacene deposition (Figure 4B), the 3D island shape persists; however, the dendritic branches extend so that the valleys are mainly present in between adjacent islands. This means that vacant volume between the individual branches starts to fill. At the same time, the roughness increases to $\sigma_{\text{RMS}} = 8$ nm, and the maximum in the inclination distribution moves to about 1° (Figure 4D, blue line). In a closer look, areas are observed which are at lower level with respect to the surrounding terraced areas (see Figure 4E). This deviating effect is more pronounced when inspecting the amplitude or phase images. There, these areas appear to have a very similar effect on the cantilever amplitude and phase change but with the edges, i.e., the transition from one area to the other, being clearly visible. In addition, such areas are located in areas where two dendritic branches start coalescing, and this lower level area seems to be in the connecting volume between these branches.

For the case of the 300 nm nominal thickness film, additional features appear (Figure 4C). In some areas, the dendritic three-dimensional islands are still found and comparable to the 100 nm film. Surprisingly, there is another common structure now apparent in the AFM micrograph. Alongside the dendritic islands, structures with a pyramidal shape and heights
significantly larger than any island structure (100–200 nm) are observed. This is also mirrored in a strongly increased mean-square roughness, which is now at $\sigma_{\text{RMS}} = 75$ nm. Most of the pyramid bases have deltoid-like shapes and form a close contact with the adjacent layers so that a depletion region between these structures is absent. Height profile extraction shows that all these pyramids are self-similar, with similar slopes for the different facets (cf. Figure 4F, line scans below the 300 nm height image). Common inclinations with the surface range between 19° and 24°, suggesting that each pyramid is the result of a pentacene single crystal with an orientation different to those where the 001 plane is parallel to the substrate surface. Also, the incline distribution (Figure 4D, black line) shows, next to an increased maximum to 3°, an additional bump coming up between 10° and 20°, most likely originating from the pyramid growth. In fact, the GIXD measurements show the presence of another phase, with the 001 plane inclined by 21° from which it can be followed that these pyramids correspond to these GIXD features.

**DISCUSSION**

Numerous studies on pentacene film growth have been performed, mostly focusing on the behavior at the film–substrate interface, i.e., the region where the growth is dominated by the thin-film phase. However, in the thickest evaluated films in this study (300 nm nominal thickness), a bulk phase polymorph with a tilted orientation of about 21° is identified by the evaluation of the GIXD map (cf. Figure 3C). Further, this second bulk phase was previously described as the so-called Holmes phase. This second bulk phase is commonly observed from pentacene single crystal growth and was suggested to be unstable in thin films on silicon surfaces, which, at least over a timespan of several weeks, can be ruled out here. This suggests that the presence of the other phases or the use of specific preparation parameters within our experiments allows for a stabilization of the Holmes phase also within films as thin as 300 nm. The corresponding AFM measurements reveal a new morphology in the form of steep and high pyramids (cf. Figure 4C). All of these pyramids have facets with inclinations between 19° and 24° with respect to the substrate. This angle correlates well with the inclination of the Holmes phases identified in the GIXD pattern. It should be noted that some pyramids occasionally appeared in thinner films of just 100 nm nominal thickness meaning that these structures are already initiated for thin films where the pentacene thin-film phase still dominates the film growth. Earlier reports show that this tilted bulk phase even can occur in 20 nm thick samples but compared to our samples at significantly higher substrate temperatures. In any case, the growth of the Holmes phase is favorable which can be followed from the very large extension (more than 200 nm in height) with respect to the surrounding materials, which at high coverage results in the formation of closed structures.

The experimental findings raise the question why the Holmes phase occurs with its 001 plane tilted by approximately 21° to the substrate. An inspection of the molecular arrangement of pentacene molecules in the unit cell of the thin-film phase and the Holmes phase shows that in both phases molecules pack in a herringbone motif. One difference is, simply put, the inclination of the molecules with respect to the 00L contact planes. Having a molecular alignment of molecules in the Holmes phase with the upright-standing molecules in the thin-film phase rationalizes the occurrence of the Holmes phase with a specific inclination (cf. Figure 5B). Therefore, the thin-film phase islands most likely provide nucleation sites for the Holmes phase. For this Holmes phase
nucleation, the intralayer molecular packing within the thin-film and Holmes phases, or more specifically the herringbone pattern, remains nearly unaffected at the contact of these two phases. It should be noted that an alignment of molecules in the Holmes phase with molecules in the Campbell phase leads to very different tilt angles and would not explain our experimental findings.

The fact that this phase transformation appears, for the presented sample series, only in thicker films and the relatively large inclination angle of 21°, suggests that nucleation is occurring on top of thin-film phase mounds. The inherent thin-film phase island shape with relatively sharp tips together with some positional freedom due to the lack of extended neighboring terraces points toward this explanation. It also highlights that, for the current sample series, the thin-film phase is not entirely capped by the Campbell bulk phase over time, as otherwise no nucleation center would be available for the pyramids to grow. It should be noted our film preparation at room temperature and the nucleation at the film surface are reasons that the Holmes phase nucleates in this study instead of the Campbell bulk phase in later stages of film growth.16

The Campbell bulk phase polymorph is first found in samples of at least 50 nm thickness. We could not find any indication in the experiments that crystallites in the Campbell bulk phase were present in films of just 20 nm. Note that for samples prepared at higher substrate temperatures, it was previously suggested that the Campbell bulk phase growth already starts at the interface with the substrate during the very early stages of film growth.16 On the appearance of the Campbell phase, our experiments show that its crystals assemble either with the 001 planes of bulk and thin-film phase in parallel (Figure 5A) or with the 001C planes inclined by 0.75° to the substrate surface (or the thin film 001T). However, as there is not enough information to identify a certain growth mechanism for the tilted Campbell phase crystals, a reason for their development remains unclear. The amount of the "parallel" Campbell phase (cf. Figure 2B, observed at Δω = 0°) and the amount of the "inclined" material (cf. Figure 2B, observed at Δω = ±0.75°) can be estimated from their respective diffraction intensities. While the diffraction intensity of parallel species is represented by the rocking scan, the value for the inclined phase needs some more consideration. A single rocking curve at a specific azimuthal angle of the inclined phase reveals two peaks, showing that two kinds of crystals exist, which are either 0.75° or −0.75° inclined. For other azimuthal directions this is very similar, which means that all these diffracted intensities need to be taken into account; i.e., the intensity for a full 360° needs to be summed. Doing such an analysis, it can be estimated that the inclined pentacene bulk phase species is about 30 times more common when compared to the parallel crystallite portion; the 0.75° tilted portion is the majority species and, thus, dominates the bulk phase formation in these pentacene thin films. It is surprising that this behavior has not been described previously, but as other studies often employ either rocking curves only on the thin-film phase peaks or use only GIXD measurements, this subtle inclination was most likely hidden rather than not present. The reason for the development of these inclined Campbell phase crystals is, however, not fully clear. AFM analysis shows that flanks defined by various pentacene terrace steps have a steepness in the range of 0.3°−2° (cf. Figure 4D). This may suggest that this steepness corresponds to the 0.75° tilt of Campbell phase crystals, or in other words, the crystals grow along the contours of thin-film phase islands rather than within a single terrace. This agrees well with recent findings of the pentacene bulk phase needle-like crystals, growing down/up a thin-film phase island.22

This raises the question, what initiates the Campbell phase formation? In general, deposition of low nominal thicknesses of pentacene on silicon surfaces results in the formation of dendritic islands in the thin-film phase. Here, the island shape is dictated by limited surface diffusion ("diffusion-limited aggregation" or DLA).42,50 This DLA type of growth means the simultaneous formation of various branches. As more material is deposited, the islands increase in size and height. This also means individual branches start to coalesce (cf. Figure 4A). As defects are incorporated in the island structures as shown previously,38 this hinders the development of extended single-crystalline areas between branches of a thin-film phase island. In a standard AFM height scan of films containing solely the thin-film phase (e.g., Figure 4A) or a combination of thin-film and Campbell phase (e.g., Figure 4B) there is not much difference observable. However, the optical scanning near-field IR investigations of a very similar film, enabled detection of the position of elongated Campbell phase structures.22 In addition, the authors combined their findings with AFM imaging showing that there is a small, but noticeable, “disturbance” within single terraces best identified by amplitude or phase contrast information. This compares very well with our findings (cf. Figure 4). In transmission electron microscopy this area is noted as a concave transition region between the two phases.25

Comparing the location of these elongated Campbell phase crystals (needle-like) with the surrounding thin-film morphologies indicates that the needles are most likely located in the area where two branches are unable to coalesce. In general, a formation of stacking faults means continued growth would result in a large amount of stress developing, which is energetically unfavorable. In the case of the thin-film phase, this limits its further growth, at least in some areas of the island, by formation of so-called hollow cores,38 i.e., empty areas in the center of a screw dislocation formed to avoid stress energy. From simple considerations it can be followed that pentacene molecules arriving at such a site might prefer to nucleate in their lowest energy state,27 which in this case means Campbell phase formation is most likely to happen in the areas of the stacking faults. From these results we suggest that, at least for the present case, the Campbell phase cannot grow from the very interface, except in the case where thin-film phase growth is impeded by defect formation.

In turn, this might suggest that a defect free thin-film phase crystal will likely not transit into the Campbell phase as a function of film thickness. In fact, in this case, the thin-film phase continues to grow up to film thicknesses of 300 nm and may grow even further, which contradicts any assumption that formation of the Campbell phase completely limits the growth of the thin-film phase. As the number of branches in a thin-film phase island is small, this only allows for some pentacene to crystallize in the Campbell phase while other "defect free" volumes continue growing in the thin-film phase. As islands extend further from the surface, the thin-film phase provides the sites for a transition into another bulk polymorph to take place, as discussed above. This means that, for the present samples, the thin-film phase will inherently limit its own growth by assisting in the formation of other phases (Campbell or Holmes).
**CONCLUSION**

In this work, by employing a thickness-dependent growth study of pentacene together with the various previous experimental reports, plausible explanations for the occurrence of the different polymorphs in pentacene thin films were developed. By combining the results presented here with similar examples from literature, two possibilities have been suggested for the formation of the Campbell phase domains: (i) the majority of Campbell phase crystals either adopt to characteristic thin-film phase island surface slopes (where the slope angle of thin-film phase islands and the tilt of the Campbell phase 001 plane can be correlated), or (ii) the Campbell phase nucleates at stacking fault sites between adjacent dendritic branches in thin-film phase islands, as discussed in relation to the literature. The formation of the Holmes bulk phase polymorph results from the thin-film phase acting as a template for Holmes phase nucleation. In particular, a close contact of the herringbone packing in the thin-film and the Holmes phase requires the Holmes phase to tilt by 21°, which was verified using grazing incidence X-ray diffraction. This large inclination is, in addition, limited by geometric considerations; i.e., it is only possible at thin-film phase island sites with steep slopes. In any case, the thin-film phase growth is self-limiting as defects develop or some lattice sites (at the very top of islands) provide the specific properties required for bulk crystal formation. In other words, the bulk phases form as the thin-phase film assists in their nucleation.

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**Notes**
The authors declare no competing financial interest.

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