

## Growth process control of pentacene thin films and its application in full organic thin film transistors

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### Abstract

Due to its outstanding carrier transport capabilities pentacene is a prominent candidate for the active semiconducting layer in organic thin film transistors. This compound crystallizes in a layered structure with herringbone arrangement within each layer. Pentacene appears in several polymorphic structures, which differ basically by their c-axis lengths, meaning that the angle at which the molecules adsorb relative to the substrate changes from phase to phase. Obviously the interaction of the  $\pi$ -electron systems between adjacent molecules depends strongly on the stacking nature of the molecules. It has been argued, that a smaller angle between the molecular axis and the surface normal results in a larger orbital overlap which is expected to give better carrier transport properties. Therefore it is of major interest to clarify and control the growth conditions for the different phases.

We have synthesized high-quality pentacene epitaxial thin films under different growth conditions and investigated them by atomic force, scanning electron and polarization microscopy. The aim was to identify the critical growth parameters with respect to surface quality, thickness and crystallinity of the thin films and with respect to homogeneity, size and shape of grains, ordering, substrate dependence, morphology and phase formation of the polycrystalline thin films. The polymorphic phase identification and the macrostructure of the films were determined by X-ray diffraction, whereas micro-structural differences, small impurity concentrations and the temperature dependence of the structure were investigated by Raman microscopy.

It turned out, that the growth process, the film quality and/or the phase formation are highly sensitive to the deposition rate, the choice of the substrate material, the substrate temperature, the film thickness and the purity of the source material. We observed a clear power-law dependence between deposition rate and grain size.

In order to draw a bow between the structural and the electronic properties of pentacene, thin film transistors were fabricated based on the different polymorphic phases and different dielectric and electrode materials. Organic thin film transistors (OTFT) have great potential in electronic applications. For example, they find use in sensors and a variety of simple and cheap circuits. Organic

electronics focus on implementation fields, where low costs, large area production and the use of flexible and even biological substrates are essential. It turned out, that the transistor characteristics are strongly correlated with the morphological as well as the structural parameters of the active layer, with the integrity and the dielectric properties of the insulator and with the contact resistance characteristics of the electrodes. We found a threshold-like dependence of the mobility on grain size, which can be described by a field-activated transport mechanism. Careful control of the growth process results in devices with high hole mobilities comparable to amorphous silicon, low leakage currents, high on-off ratios and reproducible trapping dynamics.

Organic dielectrics enable the use of simple processing techniques, such as spin- or dipcoating by being available in liquid or soluble form. As direct application of the former results, we present in this work organic TFTs with pentacene as an active layer, organic dielectric materials and a comparison of organic and inorganic source/drain contact materials. For structuring of the source/drain contacts shadow masks and inkjet-printing were applied and both methods are compared by the electrical characterisation and determination of the charge carrier mobility of field effect transistors. OTFTs with inkjet-printed electrical contacts show contact properties comparable to devices with inorganic electrodes, and the field-effect mobility of the all organic devices are in the same order of magnitude.

### Introduction

As shown in figure 1 pentacene is a small aromatic molecule chain consisting of five benzene rings. It is an organic p-type semiconductor with the best electric properties known so far.

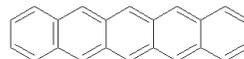


Figure 1 -  $C_{22}H_{14}$ , pentacene molecule

As pentacene is applied to the substrate by evaporation under vacuum, it tends to form well-ordered molecules in a herringbone-structure as depicted in figure 2.

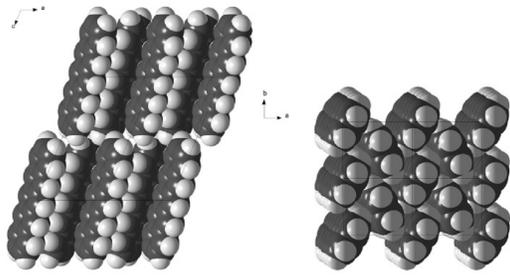


Figure 2 - pentacene herringbone structure

The polycrystalline structure, morphology and the grain quality strongly depend on a set of deposition parameters, which will be defined later.

Applied as active layer in electronic thin film devices, the advantages of pentacene are a high charge carrier mobility compared to other organic semiconductors, high on/off-ratios and the formation of highly ordered polycrystalline films.

### Thin film growth mechanisms

The basics of thin film growth have been well-described by the classification of the “initial states of film growth” published by Bauer in 1958 and are shown in figure 3:

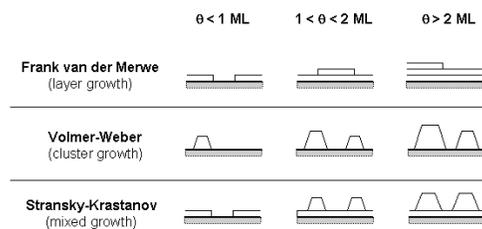


Figure 3 - initial states of crystal growth [Bauer, 1958]

The classification distinguishes the island-by-island-growth (Volmer-Weber) from the growth in layers (Frank van der Merwe). In the Volmer-Weber mode, small clusters nucleate directly on the substrate surface and then grow into islands of the condensed phase. This happens when the atoms or molecules of the deposit are more strongly bound to each other than to the substrate. This mode for example occurs in many systems of metals growing on insulators.

The layer or Frank van der Merwe mode shows the opposite characteristic. Due to the fact that the atoms/molecules are more strongly bound to the substrate, the first atoms/molecules form a complete monolayer on the surface, which becomes covered with a less tightly bound second layer. This growth mode for example is observed in the case of adsorbed gases, such as several rare gases on graphite or some metals or in several metal-metal-systems.

The Stransky-Krastanov growth mode is an interesting intermediate case; it is a layer plus

island growth. After forming the first monolayer or a few monolayers, the subsequent layer growth is unfavourable and islands form on top of the so far existing layers. There are many possible reasons for this mode to occur, and almost any factor which disturbs the monotonic decrease in binding energy (a characteristic of layer growth) may be the cause. For example the lattice parameter or symmetry or molecular orientation in the intermediate layer may not be continued into the bulk crystal of the deposit. This results in a high free energy of the deposit-intermediate layer interface, which favours island formation.

There are many examples of the occurrence of this mixed growth mode in metal-metal or metal-semiconductor compound systems and it is especially interesting for this work, because it describes the way of pentacene growth.

Assuming ideal gas conditions for the vapour deposition at an applied pressure  $p$ , the deposition rate depends on the pressure  $p$ , the molecular weight  $m$  and the source temperature  $T$ :

$$R = p(2\pi mkT)^{-1/2}$$

During the evaporation process evaporated single atoms or molecules are created and condense at the substrate. There are several processes, which can occur then, dependent on the energetic state of the atom/molecule and the substrate, as shown in figure 4.

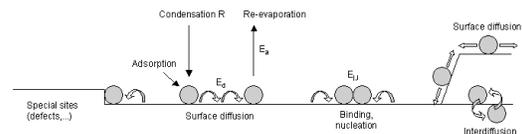


Figure 4 - Nucleation and growth on surfaces

First, the molecule can be desorbed respectively re-evaporated from the surface, which releases the desorption energy  $E_a$ . It can diffuse across the substrate with the diffusion energy  $E_d$  until it finds an energetically favourable place to nucleate or to bind. Such place can be a “special site” like a defect or an already existing cluster or island of nucleated molecules on the surface. There is always a critical cluster size or nucleation barrier, which is defined by the minimum number of molecules being able to build a stable cluster. The energy of a cluster consisting of  $j$  molecules is designated with  $E_j$ . What also can happen to the deposited molecules is an interdiffusion process with the substrate.

A final set of possibly occurring processes are such of re-arrangement. The cluster initially formed is not necessarily in its most stable form and can re-arrange in many different ways. Such processes can include shape changes caused by diffusion and/or coalescence, annealing of defects, etc. The final

morphology of the thin film is the result of all these processes.

For any evaporation and condensation process, the parameters are given by the “rate equations” relating the grain density  $N$  and the deposition rate  $R$ , a growth determining constant  $p$  and the total energy  $E$  of the system.  $p$  is defined by the critical nucleus size  $i$  of the deposited material.

$$N \propto R^p e^E$$

Roughly spoken there are three regimes of condensation:

Regime	Parameters $p, E$
extreme incomplete	$p = 2i/3$ $E \cong 2/3 \cdot [E_i + (i+1)E_a - E_d]$
initially incomplete	$p = 2i/5$ $E \sim f(E_i, E_a, E_d)$
complete	$p = i/(i+2.5)$ $E \cong (E_i + iE_d)/(i+2.5)$

Complete condensation occurs if all atoms/molecules arriving at the substrate stay there (by binding or nucleation). Therefore there is no desorption energy  $E_a$  in the total energy equation, re-evaporation from the substrate is neglected.

Extreme incomplete condensation describes the opposite case, when re-evaporation plays an important role.

In between the complete and the extreme incomplete regimes, there is a regime which often occurs in practice. In this case condensation is incomplete, but clusters capture atoms by surface diffusion. By the time the coalescence stage is reached, we may well effectively have complete condensation.

The following two pictures show examples for extreme incomplete (figure 5) and initially incomplete (figure 6) condensation of pentacene.

Figure 5 shows pentacene grown on Au under ultra high vacuum conditions ( $10^{-10}$  mbar) near the thermodynamic equilibrium, the nominal layer thickness is 100nm. In face of this high thickness, not even the first monolayer has been completed.

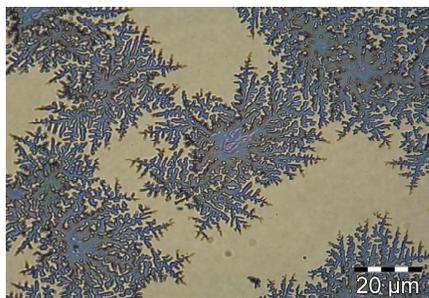


Figure 5 – extreme incomplete condensation

In figure 6 the example of evaporation under high vacuum ( $10^{-6}$  mbar) is shown. Only 4.8nm thickness lead to a complete first monolayer and 5 to 6 further monolayers grown on top.

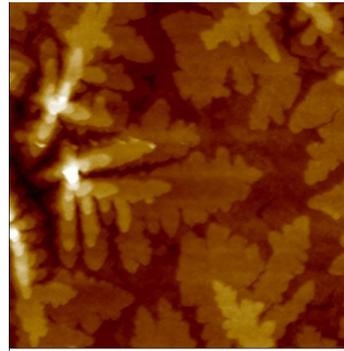


Figure 6 – initially incomplete condensation

In general – as already could be seen in figure 6 - pentacene crystallites are composed of terraces formed by single molecules bound to each other in herringbone structure. In the thin film phase, the height of one molecule and therefore of one layer is around 1.5nm, as demonstrated in the following height measurement (figure 7).

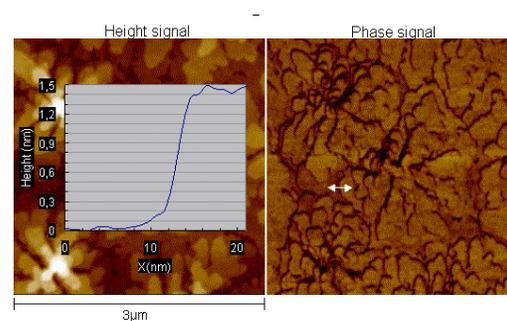


Figure 7 – step height of pentacene terraces

### Characterization of pentacene thin films

The first step in analysing pentacene thin films is the investigation of the morphologic properties primarily with the atomic force microscope, but also with the SEM and optical microscope. The phase information is obtained by x-ray diffraction and Raman-measurements. From Raman we also get data about possible impurities in the deposited material.

The electrical properties like charge carrier mobility or on/off-ratios are obtained from electrical measurements of active electronic devices.

Pentacene crystals are able to assume a wide range of different shapes on substrates. The important parameters for the morphology and in general for the structure of pentacene thin films are the substrate material and substrate treatments (chemical or physical), the substrate temperature during the evaporation, the deposition rate and the final film thickness. The purity of the original material is important for controlling this rate during the whole evaporation process. Potentially it is

necessary to do preliminary purification steps of the basic material before deposition.

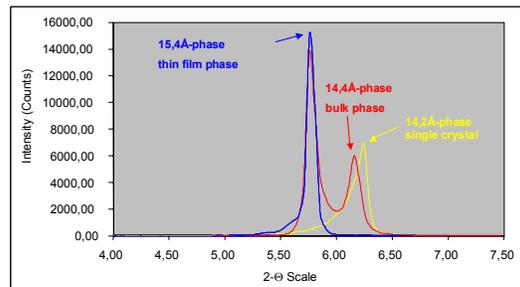


Figure 8 – XRD-characterization of pentacene thin films

In figure 8 results of X-ray-diffraction measurements on pentacene can be seen. Three curves define three different phases: the thin film (blue) and the bulk phase (red) and a third phase which can be related to the single crystal form (yellow). The thin film phase is also defined as 15.4Å-phase, which means, that in this phase the herringbone structured pentacene molecules in the film form a certain angle to the base plane, which results in a layer height of 15,4Å. The charge carrier mobility of the bulk phase is evidentially lower than the mobility of the thin film phase. For this reason the deposition parameters have to be chosen to result in a thin film phase fraction as high as possible.

#### Influence of deposition parameters on thin film morphology

In figure 9 pentacene thin films (50nm) evaporated on SiO<sub>2</sub> at different deposition rates are shown:

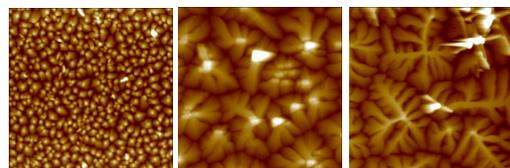


Figure 9 – influence of deposition rate, (a) 0,6ML/s, (b) 0,1 ML/s, (c) 0,04 ML/s

It is clearly visible that decreasing the deposition rate not only increases the grain size but also changes the surface morphology of the films from an assembly of squared to one of ramified grains. Grain density decreases with decreasing deposition rate.

Figure 10 shows the result of a number of analysed evaporation experiments and describes the grain density versus the deposition rate. The dependence of the grain density on the deposition rate can be described by the rate equations. For pentacene the critical nucleus size  $i$  is 3, hence for initially incomplete condensation the factor  $p = 2i/5 = 1.2$ . For pentacene the theoretical grain density  $N = R^{1.2}$ . The measured value is 1,279.

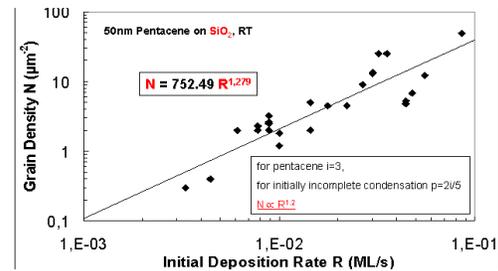


Figure 10 – Grain density vs. deposition rate

Figure 11 shows the influence of the substrate material on the pentacene thin film morphology. 50nm pentacene has been grown on different substrates under high vacuum at a substrate temperature of 65°C and the same deposition rate.

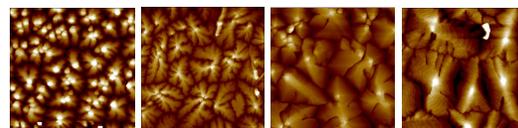


Figure 11 – Influence of substrate material, (a) SiO<sub>2</sub>, (b) PMMA, (c) PVP, (d) PVCi

There is a number of substrate materials that, due to their specific physical interaction with the condensing molecules, are a good basis for the formation of polycrystalline films with high molecular ordering. In this case the topography of the films resembles a mountainous region composed of well separated, ramified grains. Although the branched shape of the crystallites is typical for pentacene films grown on SiO<sub>2</sub> (Fig.11a), which is a very smooth substrate (RMS roughness = 0,15-0,2 nm), a lot of organic materials ranging from dielectric to conducting doped polymers also support the formation of overlapping, ramified grains (Fig.11b-d). PMMA or PVCi substrates have a slightly higher RMS roughness of 0,2-0,5 nm, the roughness of PVP, however, is about 0,15-0,3 nm which is comparable to the one of SiO<sub>2</sub>.

In figure 12 the influence of the substrate temperature on pentacene thin films on SiO<sub>2</sub> is depicted:

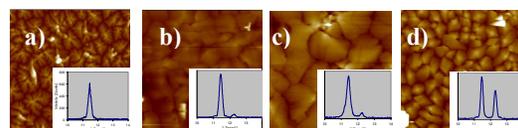


Figure 12 – Influence of the substrate temperature (pentacene on SiO<sub>2</sub>), a) 25°C, b) 60°C, c) 65°C, d) 75°C

An increase of the substrate temperature during the condensation process usually leads to an increase in the average and the maximum grain size. This is due to the fact that for higher temperatures  $T$  the mobility of molecules arriving at the surface is

increased resulting in a better alignment of the molecules, a faster edge diffusion and a lower nucleation density.

The correlation between substrate temperature and grain size is not fully understood because other processes are also influenced by the temperature. Thermal desorption plays a role together with temperature-induced phase transformation processes and changes in the volume fraction of the different pentacene phases. This latter effect may be the reason for the reduced grain size and shape observed at the film deposited at 75°C compared to the one at 65°C. At 75°C the crystallites are rather square and obviously smaller than for the deposition at 65°C, where the grains show a ramified shape.

The substrate temperature during the evaporation process thus influences the grain size, but as can be seen from this experiment, this behaviour shows a threshold around 65°C. With increasing substrate temperature the bulk phase fraction strongly increases. Out of these measurements the optimum substrate temperature for pentacene thin films on SiO<sub>2</sub> was appointed to 65°C.

The **film thickness** is another important parameter that is related to the formation of the two-phase system. Increasing the film thickness does not only increase the bulk phase fraction but also decreases the grain size. In general for applications of organic thin film transistors it is not necessary to use high layer thicknesses (>50nm) because the charge carrier transport takes place in the first few monolayers near the dielectric-semiconductor interface.

### Organic active electronic devices

With regard to device applications the key question is how the different pentacene morphologies and phases differ with respect to their charge carrier transport properties and, most important, what are the mobility values to be assigned to the different phases. Therefore we investigated the electrical properties of a large number of thin-film transistors, that were constructed in the common-gate configuration with source and drain on top.

We use three designs of bottom-gate, top-source/drain-configurations with different combinations of organic and inorganic materials shown in figure 13.

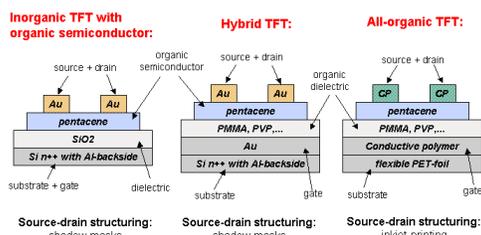


Figure 13 – TFT designs; bottom gate, top source/drain

In the first described design on the left, the only organic part is the semiconductor pentacene. Normally the substrate consists of highly doped silicon which is metallized on the backside, the dielectric is SiO<sub>2</sub>, the source/drain material is gold. We use this configuration to investigate the influence of any pentacene deposition parameter changes on the electrical properties of the final device.

When making experiments on the interplay between organic dielectrics and pentacene, we use the second configuration designated as “hybrid TFT” or similar ones. Roughly spoken we substitute SiO<sub>2</sub> by the organic dielectric.

In figure 3 you can see a possible design for an all-organic TFT, we already successfully produced and characterized. It consists of a flexible substrate (for example PET), coated with a conductive polymer as gate material. The organic material can be for example PMMA or PVP. The source/drain material again is a conductive polymer, in this case structured by inkjet printing.

For the first two designs examples will be shown. An example for an all-organic TFT will be presented in the appending talk at Polytronic 2004.

In figure 14 the output characteristics of a SiO<sub>2</sub>-pentacene-TFT can be seen:

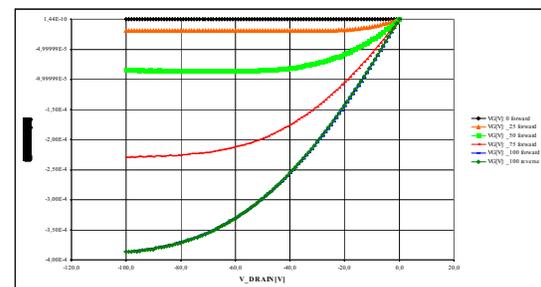


Figure 14 – Output characteristics of SiO<sub>2</sub>/pentacene-TFT

The on/off-ratio is  $7 \times 10^6$ , which is very high for pentacene transistors, the saturation is distinct, the hysteresis is weak. The reached drain current for -100V gate-voltage is around  $10^{-4}$ A.

The calculated charge carrier mobility was calculated to  $0.55 \text{ cm}^2/\text{Vs}$ .

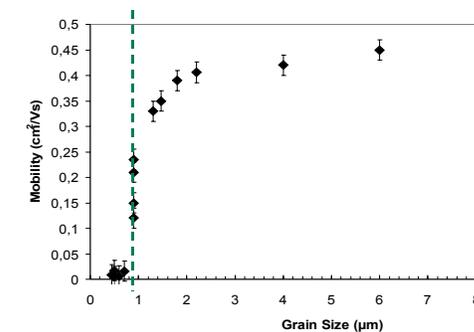


Figure 15 – Mobility vs. Grain size

In figure 15 the relation between charge carrier mobility and grain size for pentacene thin films on SiO<sub>2</sub> is depicted. If the pentacene layer of a transistor consists of grains with average size below 1 μm then the mobility is very low (~ 10<sup>-2</sup> cm<sup>2</sup>/Vs). For polycrystalline films with grains of 1 μm one observes a steep increase in the mobility, which levels for larger crystallites. Such a threshold behavior can be expected if the carrier mean free path is about 1 μm resulting in increased surface scattering and grain boundary effects for fine granular layers. Above this threshold an increase in grain size does not drastically increase the mobility (about a factor of 2-3).

As example for a “hybrid TFT”, consisting of organic semiconductor and gate dielectric, but inorganic electrodes, the output characteristic of a transistor with the organic dielectric material PVP is shown in figure 16.

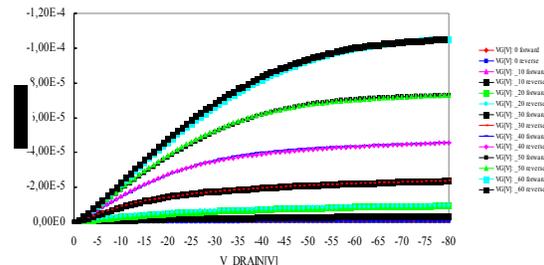


Figure 16 – Output characteristics for a PVP-pentacene-TFT

The output characteristics show again good saturation, the reached drain-currents are in the same range as shown for SiO<sub>2</sub>. It has to be considered, that the maximum applied gate voltage here is 60V compared to 100V for SiO<sub>2</sub>. The on/off ratio is 1,5 orders of magnitude lower as measured for the SiO<sub>2</sub>-TFT, namely 2x10<sup>4</sup>. Only a very low hysteresis behaviour can be observed. The measured charge carrier mobility for this hybrid TFT is even a little higher than for the SiO<sub>2</sub>-TFT, 0,65.

### Conclusion

We have shown that precise control of the growth process and the growth conditions of pentacene thin films by adjusting the parameters substrate material, substrate temperature, deposition rate and film thickness result in films with specific granularity (grain size), surface morphology and phase distribution. The growth mode is a multilayer (3D) island growth mode for substrates that are sufficiently inert to the arriving molecules.

In general, there is a number of materials being a good basis for the formation of polycrystalline pentacene films with high molecular ordering, as shown for SiO<sub>2</sub>, PVP, PMMA and PVCi.

By decreasing the deposition rate the maximum grain size increases, following a potential law with the grains becoming more ramified. Moreover, the

volume fraction of the thin film phase, where the molecules form the largest angle to the substrate, increases with respect to the one of the bulk phase. The substrate temperature also strongly influences the grain size as well as the bulk phase fraction. The increase of the grain size with increasing substrate temperature shows a threshold behaviour around 65°C. This is true for all types of substrates used in this work.

Increasing film thickness does not only increase the bulk phase fraction but also decreases the grain size.

The electrical characterization of the films by measuring the transfer characteristics of pentacene-based thin-film transistors indicated that the dependence of the mobility on the grain size shows a threshold behavior revealing a mean free path of 1 μm for the charge carriers.

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