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# TIPS-pentacene crystalline thin film growth

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ABSTRACT

The crystalline film growth of TIPS-pentacene thin films by confined solution deposition is investigated. The crystalline thin films grow dendritic in the initial stage and continue to grow to elongated plate-like crystals when the solution is deposited in a confined space in-plane. The majority of the thin film, containing smaller thin crystals, is formed within the first 10 s after depositing the solution and continues to grow in minutes to millimeter sized single crystals. By atomic force microscopy we show that impurities are expelled by the growing crystals and clusters accumulate at step edges on the surface of the larger crystals. The influence of crystal thickness and orientation on the electronic transport in field-effect transistors is studied, and shows an optimum performance for devices with thin elongated crystals that are aligned parallel to the electric field between the source–drain electrodes.



## 1. Introduction

Organic field-effect transistors (FETs) are key electronic components for future flexible organic electronic devices [1–4]. The highest field-effect mobilities reported for organic materials are those obtained from single crystal devices [5–8]. Recently, a lot of effort has been given to fabricating crystalline organic semiconducting thin films from solution for the use in FETs [5,9,10]. Fabricating organic crystalline films from solution offers the advantages of non-vacuum processing at low temperatures, which is potentially low-cost and can be applied to make large-area flexible electronics. Furthermore, the emergence of new processes and materials for the fabrication of single crystal devices from solution resulted in field-effect mobilities higher than 10 $cm^2/V$ s [5,11]. Several groups have focused on a soluble pentacene derivative, 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene, as the semiconducting material in organic FETs, since it can grow crystalline thin films from solution, composed of large single crystal domains and demonstrates excellent semiconducting behavior [9,12–15]. The reported field-effect mobility in TIPS-pentacene ranges over several orders of magnitude and can be as high as ~1 $cm^2/V$ s [9,14,16–19]. The hole mobility in TIPS-pentacene is largely dependent on crystal orientation and crystal quality, *i.e.*, the size of the single crystal domains, the presence of cracks and the crystal thickness [9,13,17,19]. These parameters are influenced by the choice of solvent, concentration, annealing temperature and deposition method [14,18]. In general, the highest field-effect mobilities are obtained from high boiling point solvents and slow crystal growth or from a binary mixture of solvents [14,19–21]. However, to completely remove a high boiling point solvent from the thin film, annealing is required. Annealing above 60 °C degrees was shown to introduce cracks in the crystalline TIPS-pentacene films and, thereby, limiting the performance [22]. We have recently demonstrated a versatile method to fabricate single crystals and crystalline films of organics by means of so-called confined solution deposition (CSD) [23]. Due to a confined space in-plane, by limiting the vertical direction, crystalline organic thin films can be grown from low boiling point solvents at room temperature. Thin films of

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TIPS-pentacene were shown to grow into large crystals from chloroform by CSD [24]. For TIPS-pentacene different crystal morphologies were observed on a single substrate, making thin films fabricated by CSD suitable for studying the effects of crystal quality on transistor performance. Perfluoropolyether (PFPE) stamps on top of the substrate were used to create the confined space between the substrate and stamp. Since these stamps are transparent, we can observe the crystal growth *in situ* by optical microscopy during the formation of the film. In this report we study the crystal growth of TIPS-pentacene in more detail by CSD. We relate crystal growth and quality to transistor performance. Furthermore, the elongated radial crystal orientation in the film enables us to investigate the charge transport anisotropy in TIPS-pentacene crystals.

## 2. Results and discussion

Previously, we published the fabrication of perfluoropolyether (PFPE) stamps in a mold of photoresist with a line pattern used for the deposition of solution in a confined space [23,24]. The limited adhesion of the PFPE stamp to the substrate is exploited to create a confined space. The stamp was pressed locally with two lines onto a substrate to ensure a good adhesion to the substrate at the sides of the stamp, see Fig. 1a. Between these two lines in contact with the substrate, a third line was left untouched and did not adhere to the sample, creating locally a confined space of submicron dimensions (hereafter called the channel) between the substrate and stamp. The exact spacing between the stamp and substrate is unknown and will, likely, vary slightly from sample to sample. The solution of TIPS-pentacene in chloroform was deposited by capillary forces underneath the stamp. Due to the confined space in the channel region, this area had the fastest uptake of solution. The deposition of solution in the reservoirs next to the channel has no noticeable effect on the film formation, *i.e.*, deposition of the solution solely in the confined space leads to similar crystalline films. After the evaporation of the solvent, a thin film of crystalline TIPS-pentacene was formed in the confined space, indicated by the red area in Fig. 1a. After drying the stamp is peeled off and the crystalline thin film was analyzed and/or Au source–drain electrodes were thermally evaporated to complete the field-effect transistors.

The resulting TIPS-pentacene thin film consists of large elongated single crystal domains, which can be up to 5 mm in length. Fig. 1b shows a stitched image of several optical micrographs. Fig. 1c shows the same image by cross polarized light microscopy. The feather-like crystal domains cover almost completely the area defined by the channel region of the stamp. Initially, the crystal domains grew dendritic in all directions from a nucleation point (location **1**, Fig. 1b), but due to the elongated shape of the channel the main growth direction (indicated by the arrow in Fig. 1c) of the crystal domains aligned, where they continued to grow into larger plate-like crystal grains.

A close-up image of the crystalline thin film around a nucleation point is shown in Fig. 2a, where by polarized light microscopy the different crystal orientations are visible by their different contrasts. Upon rotation of the sample, these contrast invert, indicating that the difference of contrasts between near regions is due to their different crystalline orientations. Around the nucleation point most crystal domains are short and branch at several locations, indicative of high supersaturation and thus a fast growth rate. Towards the end of the film, the crystalline film continues to grow, but at a slower rate to form large single crystal domains (Fig. 2b). When observed under cross polarized light, the color gradient in these single crystal domains indicates a change in crystal thickness towards the end of the film. In the online supporting information a movie is available showing the crystallization underneath a stamp with a channel width of 2 mm. The PFPE stamp on top of the substrate is transparent and allowed for the *in situ* observation of the crystallization by cross polarized light microscopy through the stamp. Every frame of the movie is about 6 s in real time, due to the long exposure time that is required when taking an image under cross polarized light at a low magnification (25×). In the first 10 s after depositing the solution, the majority of the film has already crystallized. The crystal regions continue to grow unidirectional towards the edge of the stamp for the next 2 min at a slower rate, resulting in aligned and large crystal domains.

To further investigate the different crystalline regions and their electronic properties, we fabricated FETs by

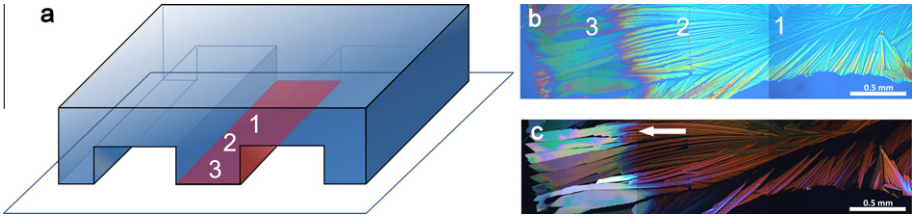


**Fig. 1.** Schematic drawing of the PFPE stamp on top of the substrate for confined solution deposition (a). The sides of the stamp are physically pressed onto the substrate for good adhesion. The channel region in the middle (indicated by the red area) is not adhering to the substrate and forms a confined space of submicron dimensions where TIPS-pentacene crystallizes into a film from a solution, with single crystal domains of a few millimeters in length. (b) A stitched image from several optical micrographs of a crystalline TIPS-pentacene film. Several crystalline regions are defined in panel (a) and (b); the center region (1) where crystalline domains are small and branched, the transition region (2) with long elongated crystalline domains, and the outer region (3) with plate-like crystalline domains. The crossed polarized image (c) of the optical micrograph in (b) shows the elongated crystalline regions in the film. A color gradient is observed due to a varying crystal thickness. The crystal growth direction is indicated by the arrow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)