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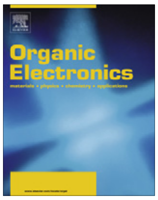

Fabrication of organic semiconductor crystalline thin films and crystals from solution by confined crystallization

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ABSTRACT

Highly crystalline thin films of organic semiconductors processed from solution for electronic devices are difficult to achieve due to a slow and preferential three-dimensional growth of the crystals. Here we describe the development of a processing technique to induce a preferential two-dimensional crystalline growth of organic semiconductors by means of minimizing one dimension and confining the solution in two dimensions into a thin layer. The versatility of the process is demonstrated by processing small molecules (TIPS-pentacene and C_{60}) and a polymer (P3HT), all from solvents with a relatively low boiling point, to obtain crystalline thin films. The thin films show an improved in-plane packing of the molecules compared to films processed under similar conditions by spin coating, which is beneficial for the use in organic field-effect transistors.

1. Introduction

Organic field-effect transistors are of potential importance for many future electronic applications, such as displays [1,2], RFID tags [3] and sensors [4–6]. The devices with the highest field-effect mobility, a key figure of merit, are those comprising organic single crystals [7–10]. Devices based on single crystals are free of large structural defects (e.g., grain boundaries) that limit electronic transport; mobilities as high as 20 $cm^2/V\,s$ have been reported [11]. However, many techniques for single crystal devices face several limitations in processing. For example, traditional single crystal devices grown from vapor are notoriously hard to fabricate. The crystals are slowly grown from vapor in a thermal gradient furnace, visually selected and individually placed by hand on top of electrodes. This introduces a low yield and low reproducibility and, hence, makes fabrication of single crystal devices by this method unsuitable for up-scaling and implementation into existing process technology. To tackle this problem, we have previously reported processes using patterned surface modification to grow single crystals locally on top of electrode arrays [12,13]. Instead of using single crystal devices grown from vapor, crystalline films obtained from solution processing are good candidates for high performance field-effect transistors (FETs) [14–17]. The recent emergence of novel, soluble small molecules demonstrate that field-effect mobilities up to 10 $cm^2/V\,s$ can be achieved in single crystal devices from solution processing [18]. Utilizing single crystals from solution for large-area applications is challenging, but a major step forward was demonstrated by inkjet printing of single crystals by means of anti-solvent crystallization of 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT), where an average mobility of 16.4 $cm^2/V\,s$ was obtained with a peak mobility of 31.3 $cm^2/V\,s$ [19]. The fabrication of high quality crystalline films or single crystals from solution often requires a slow drying process at room temperature, due to the use

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of high boiling point solvents, after which an annealing step is required for the removal of these solvents [18,20]. A technique to fabricate oriented crystalline films from solutions with a low boiling point is solution shearing [21,22]. However, due to the formation of cracks in the film, the crystal domains are limited in size in this shearing process. A technique for the fabrication of crystalline conjugated organic nanostructures is provided by lithographically controlled wetting, where by localized deposition of a material from solution nanostructured lines are formed that duplicate the stamp pattern on top [23,24]. The crystalline organic lines have a width smaller than 200 nm and showed an improved electrical transport compared to spin coated samples of the same material. Upscaling of the method to larger areas was not presented and large single crystals cannot be obtained by this method.

Therefore, a quick and simple method for the fabrication of crystalline films or crystals to test the field-effect mobility of a material needs yet to be developed. This process should require only small amounts of material per sample and should result in uniform films. The latter implies eliminating the coffee ring effect, as is often observed in drop casting due to a gradient in evaporation speed and pinning of the material at the evaporation front.

2. Results and discussion

Here, we report a technique to fabricate organic crystalline films from solvents with a low boiling point and without annealing of the films. For the deposition of the organic semiconductor, we confine the solution in the vertical direction between the substrate and a fluorinated stamp. The fabrication process for thin films in a confined space is schematically depicted in Fig. 1. First, a line pattern was fabricated in a photoresist structure, which served as a mold for the preparation of fluorinated stamps. The lines varied in width between 1 and 4 mm and have a length between 8 and 15 mm. The stamps were fabricated according to a previously published procedure for microfluidic masters made from perfluoropolyether (PFPE) [25] (Fig. 1a). PFPE stamps were used because of its resistance to organic solvents [26], while the more commonly used polydimethylsiloxane (PDMS) swells and changes shape when exposed to most organic solvents [27]. After curing, the stamps were placed on a highly doped silicon wafer with a thermally grown oxide, functionalized with hexamethyldisilazane (HMDS). The treatment with HMDS is not a prerequisite and it should be noted that we obtained similar thin films on untreated SiO_2 and glass substrates with a lower hydrophobicity. The stamps do not immediately adhere to the surface when initially placed on the substrate. The limited adhesion of the stamp to the substrate was utilized to fabricate the confined space. To wet the substrate locally, a small force was applied by hand on the sides of the stamp (Fig. 1b), thereby limiting the region for solution deposition to be between the sides contacting the substrate. Furthermore, adhesion of the sides of the stamp ensures that the stamp remains in place while depositing the solution. Due to the limited adhesion of the PFPE stamps on the HMDS-treated SiO_2, the middle region of the stamp (hereafter called the channel) is not in close contact with the substrate and, a small space is created that is limited in the vertical direction. The relatively high rigidity of the PFPE stamps, compared to for example PDMS, is crucial for the formation of the confined space, since it prevents the adhesion in the channel region due to bending of the stamp. The exact height of the confined space is unknown and will, most likely, vary slightly between different stamps. If the features next to the channel (the reservoirs) are not present, i.e., a flat stamp without any features, the whole stamp would wet the surface after pressing only a corner of the stamp. The reservoirs (as indicated in Fig. 1c) next to the channel region create the possibility of non-wetting and, therefore, a confined space between substrate and stamp.

Next, the solution of an organic semiconductor is deposited underneath the stamp by capillary forces (Fig. 1c). Due to the confined spacing between substrate and stamp in the channel region, this region is filled with solvent first before the reservoirs are filled. In fact, albeit hard to control by hand, the deposition of solvent only in the channel region is possible and the filling of the reservoirs with solvent does not seem to influence the film formation in the channel region. After about 5 min, the solvent dries and the stamp can be peeled off to expose the crystalline thin film in the channel region for the evaporation of Au source and drain electrodes.

Several factors determined the choice of materials used in this study: the polymer, regioregular poly(3-hexylthiophene) (P3HT), and the small molecules, 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene and C_{60}. The motivation for the material is presented at the beginning of each section related to that material. Here we investigate the thin film morphology of the three compounds processed by confined crystallization, along with their electrical performance in field-effect transistors.

2.1. P3HT

P3HT is known to exhibit a strong face-to-face packing of the conjugated backbone. The morphology of the film is strongly determined by the molecular weight and processing conditions [28–31]. A recent report demonstrated the possibility for P3HT to form films with a, previously unobserved, morphology from solution processing, where oriented nanofibrils are formed when the film is dried at high vapor pressure with a substrate on top [32]. Furthermore, it was shown that the chain alignment of P3HT can be influenced by confining P3HT in plane, in nanostructures fabricated by nanoimprint lithography [33]. The strong orientation and packing dependence of P3HT on varying processing conditions render the material ideal for studying the effects of confinement in the vertical direction.

Reference films were fabricated with P3HT from chloroform to compare with those made by the confined solution deposition technique under similar conditions. The width of the channel and reservoir were chosen independently, in different ratios. Typical transfer characteristics ($V_{ds} = -60$ V) of the P3HT FETs fabricated by confined crystallization, are shown in Fig. 2a. The square root of the drain