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Letter

Organic field-effect transistors (OFETs) of highly oriented films of dithiophene-tetrathiafulvalene prepared by zone casting

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Abstract

We report on the preparation of large area coverage of well-oriented films of dithiophene-tetrathiafulvalene (DT-TTF) from solution by using the zone casting technique. The X-ray analysis shows that the molecules are highly ordered in the films with the stacking direction parallel to the substrate. We further demonstrate that it is possible to prepare organic field-effect transistors (OFETs) employing these films. The devices reveal a remarkable OFET mobility with a maximum value of 0.17 cm^2/V s. The fact that the films are prepared from solution makes these devices eminently suitable for low-cost electronics.

PACS: Semiconductor devices; Materials sciences

Keywords: Organic field-effect transistors; Thin film; Tetrathiafulvalene; X-ray diffraction

Great interest in organic devices has emerged recently due to their potential in applications in modern microelectronics [1,2]. The performance of the best organic field-effect transistors (OFETs) is of the same order as that of amorphous silicon. The highest OFET mobilities have been found for single-crystalline materials [3–8]. However, crystals are not suitable for fabricating large-scale thin films and, in order to effectively exploit organic semiconductors as active components in electronic devices, it is crucial to develop new easy methods to prepare films of these organic molecules. Most of the devices exhibiting high OFET performance are currently prepared by evaporation of the organic layer, which is a relatively expensive process [9,10]. To promote, therefore, the development and utility of organic semiconductors, there is a clear need to find

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materials that can be solution-processed and, simultaneously, achieve a high OFET mobility [11–14]. Hence, considerable effort is currently being devoted to synthesising soluble precursors or derivatives of the organic semiconductor materials (e.g. oligothiophene, acenes) [15–19]. Recently, we reported that crystals of the organic material dithiophene-tetrathiafulvalene (DT-TTF, Fig. 1) have a very high field-effect charge carrier mobility of up to 1.4 $cm^2/V\,s$ [3,4]. These crystals were formed by a simple drop casting method, making this material interesting to investigate for possible applications in low-cost electronics. Here, we report on the preparation of large area coverage of well-ordered films of DT-TTF by zone casting and further demonstrate that it is possible to prepare OFETs employing these films.

The conductivity in ordered organic materials is typically anisotropic as it strongly depends on the electronic coupling between the neighboring molecules in the different crystallographic directions. For this reason, in the preparation of organic films for electronic devices, it is essential to grow them with directed order. The zone casting technique, developed in 1981 in Łódź, was specially designed for the preparation of oriented, anisotropic layers of soluble molecular materials on substrates that are not pre-oriented [20,21]. This technique consists of the deposition of a material from solution on a moving substrate. The solution is continuously supplied to the evaporation zone by a flat nozzle, the solvent evaporates from the meniscus zone, and the solute is deposited on the moving substrate. The solution supply rate, substrate velocity, initial solute concentration, solvent evaporation rate, and crystallization rate must be optimized to obtain well-ordered films. This technique was used for the preparation of oriented networks of nanowires of tetrathiotetracene-tetracyanoquinodimethane embedded in amorphous [22] or semicrystalline [23] polymeric matrices. Aligned films of discotic hexabenzocoronenes and a TTF bearing long alky chains were also obtained by this method [24,25] and, furthermore, such films could be used for fabricating OFETs [25–27]. However, this technique has never been applied to the preparation of films based on classical low-molecular-weight organic semiconductors which are not liquid crystal materials nor have long pendant chains that promote the film ordering.

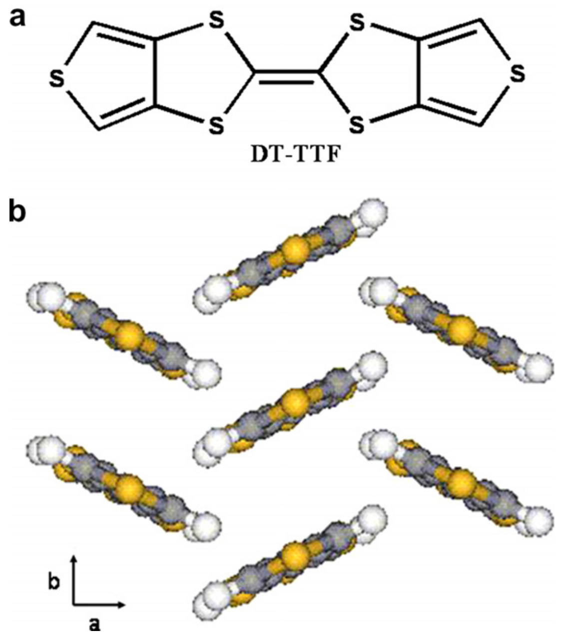

Fig. 1. (a) Molecular structure of dithiophene-tetrathiafulvalene (DT-TTF). (b) Crystal structure of DT-TTF viewed along the *c*-axis.

The high OFET performance and solubility of DT-TTF prompted us to study the preparation of oriented films of this small molecule. Zone casting films of DT-TTF were prepared from toluene solutions at concentration of 1.2 mg/ml on a silicon wafer with a 200 nm thick layer of oxide. The substrates were cleaned for one minute in nitric acid and rinsed in de-ionized water, acetone and isopropanol. The film was deposited using a specially constructed zone-casting apparatus, equipped with controlled linear stage and independently-controlled solution and substrate heaters. The solution and the substrate temperature was 60 °C. The fabrication was performed in ambient atmosphere and the substrate velocity was 30 μm/s. Fig. 2 shows an optical micrograph (taken in reflected light) of a zone cast DT-TTF film. It consists of parallel ribbons growing on the substrate along the casting direction. We were aiming at obtaining single-crystalline plates of DT-TTF on Si/SiO_2. However, DT-TTF readily crystallizes and as soon as the evaporation from the meniscus starts, many nucleation centers appear at the contact line resulting in growth of arrays of ribbon like crystals parallel to the casting direction. Between the needles the underlying substrate was observed, nevertheless, the coverage of the substrate is high. Closer inspection using AFM revealed that the crystalline ribbons are ca. 300 nm thick (Fig. 3).

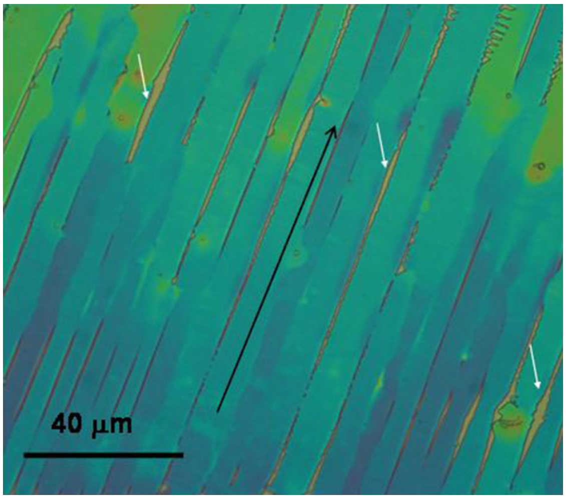

Fig. 2. Optical micrograph (reflected light) of DT-TTF films prepared by zone casting on a Si/SiO_2 substrate. The black arrow indicates the casting direction. White arrows indicate some of the places on the substrate not covered by the organic layer.

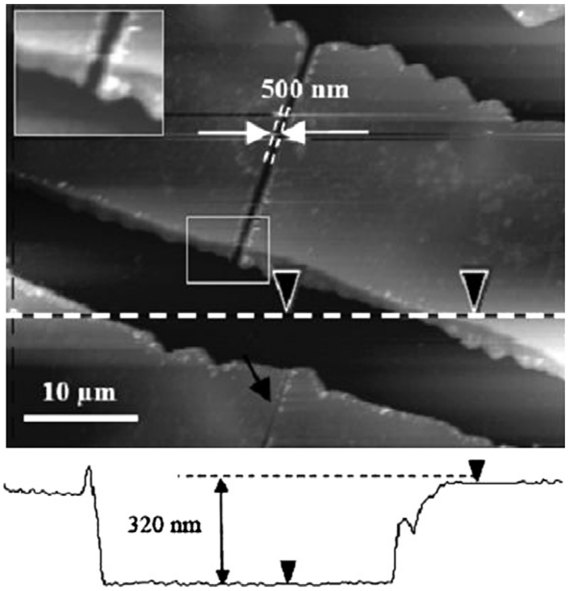

Fig. 3. AFM image of defected crystalline ribbons of DT-TTF zone cast on silicon wafer. A crack perpendicular to the ribbon going through the whole thickness is seen in the center of the image. A narrower crack in the neighboring ribbon below is indicated by the black arrow. The profile, shown at the bottom, scanned along the dotted white line reveals the thickness of the crystalline ribbons is about 300 nm.

Although the idea of the zone casting seems very simple it is rather difficult to optimize the conditions allowing the formation of layers with the desired morphology. The wetting instabilities at the solution-substrate interface (dewetting, stick-slip motion, fingering instabilities, etc.) that appear within a certain range of casting conditions lead to the formation of various morphological structures [28]. Commonly observed instability in the zone casting process is the stick-slip motion of the three-phase contact line on the moving substrate (pinning–depinning process) during the solvent evaporation. Instead of compact continuous layers, stripes of the solute perpendicular to the casting direction are formed. Under some conditions the stick-slip motion and the periodic solidification (or crystallization) along the meniscus edge occur simultaneously leading to complicated patterns. The examples of such layers obtained from DT-TTF solutions are shown in Fig. 4. The electrical properties of such layers were not investigated.

In order to study the orientation of the molecules in the zone cast films, powder X-ray experiments were performed. DT-TTF molecules crystallize forming uniform stacks along the *b* axis with an interplanar distance of 3.56 Å (Fig. 1b) [29]. In addition, the long axis of the crystals was determined to be the crystallographic *b* axis, that is, the stacking direction, which corresponds also to the conducting channel of the previously fabricated DT-TTF single crystal OFETs [3]. To develop DT-TTF films that work as OFETs, it will be essential that the molecular arrangement in the films is similar to that in the crystalline form. The X-ray powder diffraction patterns of the films indicate the presence of only (001) reflections, which points to the fact that the molecules are highly ordered with the crystallographic c^*-axis perpendicular to the substrate. This means that, similar to the high mobility DT-TTF single crystal OFETs, the stacking direction is parallel to the substrate, which is encouraging for the preparation of electronic devices.

OFETs were prepared on the zone cast films by evaporating gold electrodes on the films through a shadow mask (top-contact configuration). Devices with a channel length and width of 80 μm and 2 mm, respectively, were prepared. The study of the electrical characteristics of the device was performed in air by using the evaporated gold electrodes as source and drain contacts and the silicon substrate as a gate. Fig. 5 shows the collected mobility values, calculated in the linear regime, of various zone cast films. Due to the fact that the films were not completely homogenous along the conducting channels, we found that there was a scattering in the charge carrier mobilities obtained. The average

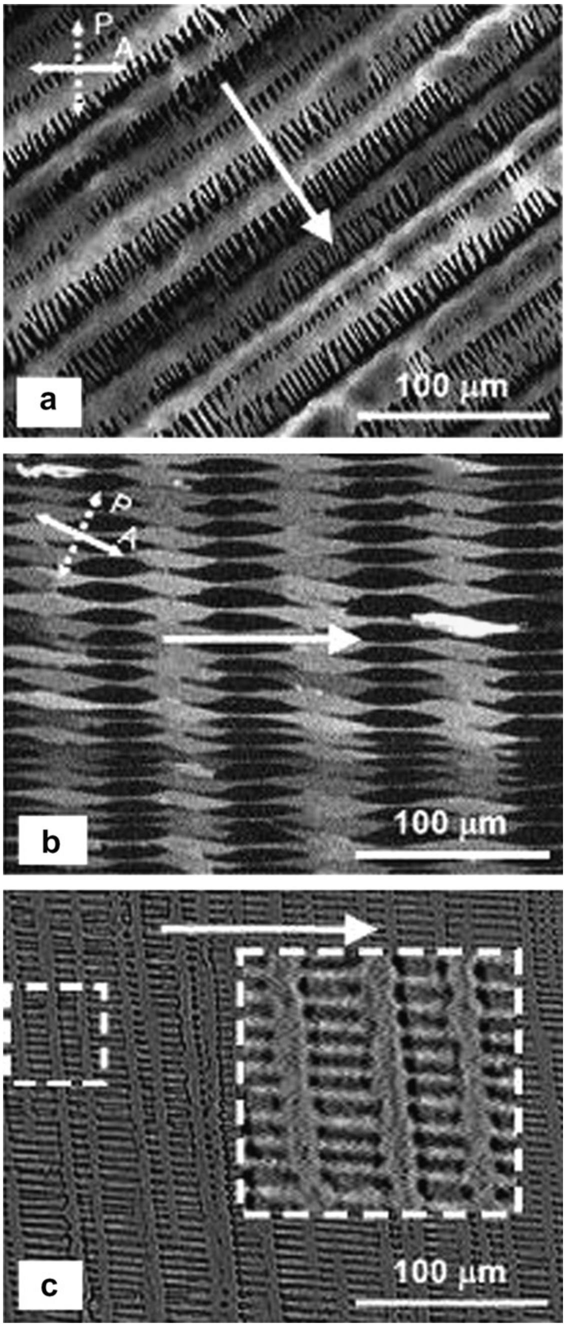

Fig. 4. Optical micrographs (crossed polarizers) of microcrystalline patterns of crystalline DT-TTF zone cast on glass from 1.2 mg/ml solution in toluene at a temperature of 65 °C, at different casting rates: (a) 6 µm/s; (b) 10 µm/s and (c) 16 µm/s. White arrow indicates the casting direction.

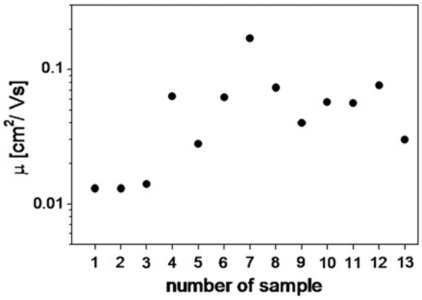

Fig. 5. Mobility values obtained for the zone cast films investigated.

mobility observed was $0.05\ cm^2/V\,s$. The highest OFET mobility found was $0.17\ cm^2/V\,s$, which is one order of magnitude lower than the maximum mobility obtained for a single crystal DT-TTF but of the same order as some of the measured DT-TTF single crystals OFETs (Fig. 6) [3,4]. In addition, we note that the intrinsic mobility of this material could be higher since it is well-known that contact resistances between organic semiconductors and metals can strongly influence the transport properties of electronic devices [30]. Fig. 6a shows the source–drain current (I_{SD}) versus the applied

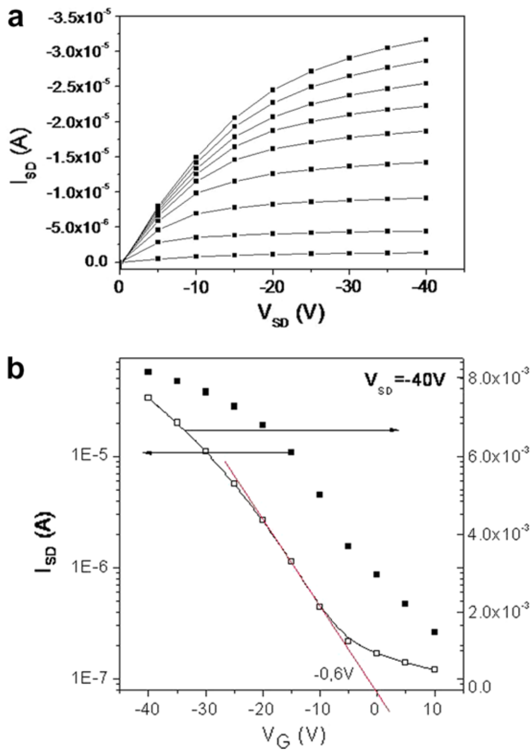

Fig. 6. (a) I_{SD} versus V_{SD} at V_G (from top to bottom) −40, −35, −30, −25, 20, −15, −10, −5 and −0 V. This device exhibited a mobility of $0.17\ cm^2/V\,s$. (b) For the same device as in Fig. 6a, I_{SD} *versus* V_G at $V_{SD} = -40$ V.

source–drain voltage (V_{SD}) across the two electrodes for different gate voltages (V_G). As expected for a p-type material [1–4], as a more negative V_G is applied, more holes are induced in the semiconductor and the conductivity increases. The transfer characteristics (I_{SD} versus V_G at fixed $V_{SD} = -40$ V) for this device are shown in Fig. 6b. The threshold voltage of this device is −0.6 V. That is, it is necessary to apply a gate voltage lower than −0.6 V to induce conductivity in the film. The devices exhibited high OFF current, probably due to the doping of the film with oxygen. We believe that this effect would be reduced if the films showed fewer defects. These results are very promising since the fact that the films are deposited from solution makes these devices eminently suitable for low-cost integrated circuit technology.

The fabrication of OFETs with a bottom-contact configuration was also attempted by performing the zone casting experiments on a Si/SiO_2 substrate with prefabricated electrodes. Unfortunately, the film formation was interrupted near the gold edges and, thus, no measurements could be performed. We believe that this was caused by the substrate inhomogeneity due to the presence of the protruding electrodes.

In summary, we successfully demonstrated that it is possible to prepare ordered films of DT-TTF from solution by zone casting. We also show for the first time the application of the zone casting technique for preparing films of low-molecular weight semiconductors. Although future work will be devoted to improve the film formation, the results obtained so far allow us to conclude that DT-TTF is a highly promising material for applications due to its facile processability and OFET performance.

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