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Inkjet printed perylene diimide based OTFTs: Effect of the solvent mixture and the printing parameters on film morphology

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ABSTRACT

In the present work, we report the influence of the solvents on the morphology and the uniformity of inkjet printed n-type (electron-transporting) perylene diimide (PDI-8CN2) semiconductor films on SiO_2 substrates. In particular, a solvent mixture composed by o-dichlorobenzene and chloroform was employed and the semiconductor crystalline structure was investigated as a function of the mixing ratio of the component solvents. For each mixture composition, the printing parameters such as substrate temperature and drop overlapping degree, were optimized to improve the reproducibility of the deposition process and the structural quality of the final films. Organic thin film transistors were fabricated and electrically characterized. The electrical measurements suggest that for the devices with larger active areas, the solvent mixture approach improves the performances of OTFTs in comparison with the use of pure o-dichlorobenzene solution.

1. Introduction

Recently, organic thin film transistors (OTFTs) have received much attention for the fabrication of low cost, flexible and large area electronic circuitry [1]. Both p-type and n-type OTFTs are required for the development of organic complementary metal oxide semiconductor (CMOS) circuits [2–4], which are able to provide electronic components with superior performances in terms of low static power consumption and higher noise margins. Different from p-channel semiconductors which have been widely studied for more than 20 years and exhibit excellent field-effect characteristics [5,6], today n-channel semiconductors are less commonly employed because of the low air stability and limited processing capability. Indeed, despite many experimental works carried out over the past few years, nowadays the number of n-channel compounds able to operate in ambient conditions with good charge mobility (μ) remains very limited. Among them, cyanated perylene carboxylic diimide derivatives are certainly the most promising n-channel candidates owing to the high μ values (0.1–1 $cm^2/V\,s$) [7,8], low sensitivity to oxygen and moisture [9,10], remarkable environmental stability [11], good solubility in common organic solvents such as toluene (TOL), chloroform (CF) and o-dichlorobenzene (DCB). In particular, this last feature opens the way to the fabrication of OTFTs by direct printing methods, like the inkjet technology, which are able to guarantee many advantages including low costs, low material wastage, selective deposition of materials and non-contact patterning [12]. In electrically active organic devices, the semiconductor morphology plays a crucial role in determining the final performances given the widely demonstrated correlation between the crystalline microstructure of the organic layer and the corresponding charge transport properties [13]. This issue is even more critical if the semiconductor is deposited by inkjet printing, since the drop drying process drastically modifies the morphology of the deposited material and can strongly affect also its overall uniformity [14]. The poor uniformity of inkjet printed films is mainly caused by the so-called 'coffee-stain' effect. This phenomenon is ruled by the convective flow occurring inside the sessile drop from its centre towards the edges, where the evaporation rate is higher, for replenishing the evaporation losses [15]. As a consequence, at the end of the drying process, the organic semiconductor results largely localized at the rim of the printed droplet. A possible approach to reduce the 'coffee-stain' effect is based on the use of mixtures of solvents with different boiling points and surface tensions. By mixing suitable high- and low-boiling point solvents, indeed, temperature and surface tension gradients can be generated producing a Marangoni flow from droplet rim to the centre (Fig. 1) [16–18]. This capillary flow balances the 'coffee-stain' effect

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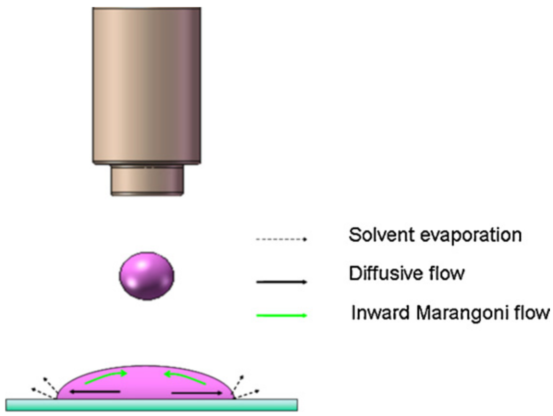

Fig. 1. Schematic representation of competing convective and inward (Marangoni) flows taking place in an inkjet printed droplet.

providing an appropriate spatial redistribution of the material. In this way, morphology and uniformity of the printed films and, more in general, the performances of the final devices can be improved by choosing the appropriate component solvents, with particular care to their volatility and surface tension properties, and their mixing ratio [17,18].

In this paper, we report the influence of the solvents DCB and CF and their mixtures on the morphology and uniformity of N,N′-bis(n-octyl)-1,6-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI-8CN_2) films which were deposited by inkjet printing on Si(gate)/bare SiO_2 (dielectric)/Au (contacts) substrates for the fabrication of n-channel organic transistors. The effect of the mixing ratio of the solvents and printing parameters (drop overlapping degree, substrate temperature) on the morphology of PDI-8CN_2 films were assessed by polarized optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The electrical response of the OTFTs was investigated through the output and transfer-curves. Mobility values were extracted from the transfer-curves and used to compare the electrical performances of devices fabricated by different DCB:CF mixtures.

2. Experimental

Inkjet printed bottom-gate bottom-contact OTFTs were fabricated on substrates consisting of a 500 μm thick highly doped Silicon (Si^{++}) layer, thin (200 nm) SiO_2 dielectric barriers and pairs of interdigitated gold source–drain electrodes. The active channels of the manufactured transistors have two possible lengths: L = 20 μm (Type I devices) and L = 40 μm (Type II devices). For all devices, however, the ratio between width (W) and length (L) of the active channels is fixed at 550. Taking into account the size of the interdigitated electrodes, the overall area printed was about 0.56 mm^2 for Type I devices and 1.65 mm^2 for Type II devices.

Before printing of the semiconductor, the bare substrates were cleaned in sequence in ultrasonic baths of acetone and isopropanol and dried with pure nitrogen (N_2) flow. PDI-8CN_2 (Polyera ActivInk N1200, Polyera Corporation) was dissolved at 6 mg/mL concentration in mixtures of o-dichlorobenzene and chloroform at different mixing volume ratios (DCB:CF 1:0, 4:1, 3:2, 1:4). The chosen solvents are the most suitable to dissolve the semiconductor material and have right volatility and surface tension properties for the inkjet printing processing (DCB: T_b = 180 °C, γ = 26.84 mN/m; CF: T_b = 61 °C, γ = 27.5 mN/m). The prepared solutions were used as inks after filtering by means of a 0.2 μm PTFE filter in order to remove possible agglomerates. The organic semiconductor based inks were deposited by means of an inkjet equipment especially designed by Aurel S.p.A. for printing inks on flexible and not flexible substrates. This printer uses the piezoelectric Drop on Demand (DoD) technology to eject droplets through Microdrop printhead (30 μm opening nozzle, 20 pL droplet volume). Moreover, the system allows to control the substrate temperature from the ambient conditions (T_{amb}) up to 100 °C. Sequences of droplets were printed at 10 Hz drop emission frequency and at printhead speed of 0.3 and 0.5 mm/s. During the printing process, the substrate temperature was optimized for each mixing ratio in order to prevent coalescence of the droplets printed on the target substrate.

Polarized optical, SEM and AFM images were acquired by Polyvar MET Reichert-Jung, LEO 1530 and XE100 Park instruments, respectively. In particular, AFM characterization was carried out in non-contact mode amplitude modulation by using a silicon nitride cantilever from Nanosensor. All electrical measurements were carried out in vacuum (10^{-4} mbar) and in dark by using Janis Cryogenic Probe-Station system connected to a Keithley 2612A Dual-Channel source-meter instrument.

3. Results and discussion

In order to investigate the effect of solvents and their mixtures on the printing quality, single droplets of PDI-8CN_2 dissolved in DCB:CF mixtures at different volume mixing ratios (1:0, 4:1, 3:2, 1:4) were printed on bare SiO_2 substrates. The possibility to use the single-solvent system (0:1 DCB:CF) was not considered, since CF low boiling point prevents to get the stable drop emission condition.

Fig. 2 reports the polarized optical microscopy images and the corresponding profilometric analyses of printed PDI-8CN_2 droplets. This figure shows that the single-solvent system 1:0 DCB:CF generates an uneven deposition of the material due to the 'coffee-stain' effect. Hence, a ring like profile, with lateral humps at the droplet rim and a thinner layer in the centre, is observed in both the optical image (Fig. 2a) and the corresponding 2D profile (Fig. 2e). On the other hand, by increasing the CF content, which has a lower boiling point and a higher surface tension than DCB, an inward Marangoni flow was generated during the droplet drying process in such a way to reduce the height of the humps at the droplet rim. This phenomenon is clearly observable in the 2D profiles of the investigated mixtures, as depicted in Fig. 2f–h. In particular, Fig. 2f outlines how the CF presence reduces the ratio between the lateral hump height and the height of the droplet centre. Moreover, it was found that the film uniformity can be further improved if a suitable mixing ratio of the component solvents is considered. Thus, the optical images and the related profilometric analyses reveal that the best condition is achieved using 3:2 DCB:CF mixture (Fig. 2c and g). At this condition, the substrate region on which the single drop was printed appears fully covered by the material, without the presence of empty zones. Finally, the further increase of the CF content (1:4 DCB:CF, Fig. 2d) leads to the formation of small crystallites spread over the printed drop region and separated each other with marked empty regions.

Organic thin film transistors were fabricated by inkjet printing PDI-8CN_2 films on Si^{++}/SiO_2 substrates with interdigitated gold source–drain electrodes. Films were obtained by printing overlapped lines (50% overlapping degree), each one realized by the sequence of overlapped drops. The lines were obtained with a drop overlapping degree of 50% and 70%, nevertheless for all the mixing ratios the optimal condition for forming uniform printed layers resulted 50%. The devices were realized with all the analyzed mixing ratios in order to investigate the effect of the drop overlapping on the printed film uniformity and, hence, on the performances of the final transistors.

In Fig. 3, the polarized optical images and the corresponding SEM analyses of the printed PDI-8CN_2 films are reported for each mixing ratio. For the mixing ratios 1:0, 4:1 and 3:2 DCB:CF, where