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Process optimization for inkjet printing of triisopropylsilylethynyl pentacene with single-solvent solutions

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ABSTRACT

Inkjet printing of 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN), a small molecule organic semiconductor, is performed on two types of substrates. Hydrophilic SiO_2 substrates prepared by a combination of surface treatments lead to either a smaller size or a coffee-ring profile of the single-drop film. A hydrophobic surface with dominant dispersive component of surface energy such as that of a spin-coated poly(4-vinylphenol) film favors profile formation with uniform thickness of the printed semiconductor owing to the strong dispersion force between the semiconductor molecules and the hydrophobic surface of the substrate. With a hydrophobic dielectric as the substrate and via a properly selected solvent, high quality TIPS-PEN films were printed at a very low substrate temperature of 35 °C. Saturated field-effect mobility measured with top-contact thin-film transistor structure shows a narrow distribution and a maximum of 0.78 cm^2V^{-1} s^{-1}, which confirmed the film growth on the hydrophobic substrate with increased crystal coverage and continuity under the optimized process condition.

1. Introduction

Solution processing of soluble conjugated molecules at low cost is a key technology to fabricate organic thin-film transistors (OTFTs) for "printed electronics". Molecular design and synthesis of organic semiconductors (OSCs) are indispensable to achieve high field-effect mobility, and numerous soluble OSCs such as side-chain-substituted acenes [1] and triethylsilylethynyl anthradithiophene [2] have been reported. The optimization of process conditions [3] or ink compositions [4] has been presented as an alternative approach toward high performance OTFTs. As the intrinsic field-effect mobility of conjugated molecules, especially that of small molecules, approaches 1 cm^2V^{-1} s^{-1} and higher values, their performances are becoming comparable or even superior to those of hydrogenated amorphous silicon (a-Si:H). Therefore, much attention is now devoted to material processing in solution forms.

In the report by Kim et al., high quality one-dimensional (1D) single-crystalline 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) microribbon field-effect transistor was fabricated by the solvent-exchange method and exhibited mobilities as high as 1.42 cm^2V^{-1} s^{-1} [5]. A similar microribbon structure was also prepared by single-drop casting on an inclined substrate [6]. High mobility bottom-contact OTFTs based on drop-cast TIPS-PEN via high boiling point solvent have also been reported [7]. More recently, devices with even higher field-effect mobilities of 4.6 cm^2V^{-1} s^{-1} were obtained by the solution shearing method at optimized shear speed [8], owing to the increased lattice strain. Therefore, a more advanced solution shearing method was proposed to achieve better control of the solution-printed film [9]. Another systematic work on process development was conducted using dip-coating method [10]. Besides the most studied TIPS-PEN, research on solution processing of other high mobility small-molecule semiconductors such as 2,7-dialkyl [1] benzothieno[3,2-b] [1] benzothiophenes has been reported. On the other hand, effects of the gate dielectric on the semiconductor processing and OTFT performance have been identified as another factor of paramount importance [11]. The introduction of ultrathin dielectric layer, such as the self-assembled monolayer molecular gate dielectric [12], would enable ultralow-power organic complementary circuits [13], however, nanometer-scale interfacial heterogeneity on the dielectric layer [14] would lead to less continuous film growth of the overlying semiconductor.

Inkjet-printed single-drop films typically possess a radial pattern of crystalline orientation [15], which would cause dramatic device-to-device differences in electrical conductivity between the source and drain electrodes of OTFTs. A promising approach for solution-

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processing of small molecule OSCs is to blend them with a polymer [16] and to print broad-area films instead of single-drop films for better uniformity in film morphology as well as improved repeatability as required for mass production. In this case, vertical phase separation [17] is essential to achieve high mobility charge transport [18] as well as improved reproducibility [19] or device-to-device uniformity [20]. Nevertheless, the highly viscoelastic polymers would sometimes make it difficult for stable jetting of the ink. Another issue is the problematic film thickness uniformity arising from the coffee-ring effect. Usage of binary solvent was reported to eliminate the coffee-ring stain in a single-drop deposition [15], however, the effectiveness seems insignificant when printing large-area films with overlapping drop assignments. Summing up all previous findings, manipulation of the substrate's surface property in conjunction with proper solvent selection seems to be a more promising solution for inkjet printing of uniform films.

In this work, inkjet printing of TIPS-PEN is performed on substrates with fine-tuned surface energies that have been obtained either by surface treatment, including molecule self-assembling and UV-ozone cleaning, or by applying a polymeric insulator that is insoluble in the ink solution, with the target of fabricating high quality large-area semiconductor films with uniform thicknesses and morphologies. The quality of the crystalline film and their interface with the insulator is studied through OTFTs in a bottom-gate/top-contact architecture. Instead of printing a blending of the OSC and a polymer, a single-solvent solution of TIPS-PEN is printed with the intension of figuring out the primary interactions between the solution and the substrate, together with their effects on film processing via the solution. In addition to the surface properties of the dielectric substrate, dependence of the electrical properties of the OTFTs on other factors including solvent selection and process parameters for inkjet printing of large-area films, such as drop spacing and line spacing, are discussed for overlapping-drop-assignment printing.

2. Experimental details

The inkjet printing experiments are performed with a Dimatix DMP3000 printer. TIPS-PEN (TCI Co. Ltd., Tokyo, Japan) is dissolved in orthodichlorobenzene (*o*-DCB, for Sections 3.1–3.4) or 1,2,3,4-tetrahydronaphthalene (tetralin, in Section 3.5) and injected into a cartridge through a 0.45 μm filter. The inkjet printing is operated with a 10 pL printhead (DMC-11610) at 1 kHz jetting frequency for a trade-off between high efficiency and stable jetting. The printer operates in a temperature-controlled ambient of 25 °C with humidity maintained at 35%. The electrical properties of the semiconductor films are evaluated with a bottom-gate/top-contact thin-film transistor (TFT) structure as shown in the schematic diagram of Fig. 1(a). An optimized 3-segment waveform as shown in Fig. 1(b) is used to fire droplets stably at a velocity of 2.5 m/s. The surface energies of the dielectric substrates are modulated by surface treatment with either self-assembled monolayer (SAM) of organosilane, UV-ozone cleaning (PSD PRO-UV10T), or spin-coating of an insulating polymer layer (MIDAS System SPIN-1200D). The surface energy is estimated according to the contact angles measured at room temperature with an OCA15 video-based automatic contact angle measuring instrument (Data Physics). Deionized water and methylene iodide are used as the test liquids. More details were described in a previous report [21]. Film morphology of TIPS-PEN is characterized with optical microscope (Leica DM2500M equipped with polarizer and analyzer) and atomic force microscope (AFM, Bruker Multimode). The cross section profile is obtained with an Ambios XP-200 profilometer. Device characteristics were measured at room temperature in ambient air using a Keithley 4200 semiconductor parameter analyzer. Field-effect mobility is extracted from the transfer curves collected in the saturation region with a V_{ds} of −60 V.

For surface modulation over a wide range, the hydrophilic SiO_2/Si wafer is firstly treated with a SAM layer of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) to obtain a hydrophobic surface with very small surface energy, both the dispersive and the polar components. The surface treatment is performed in FDTS vapor for 2 h within a vacuumed container.

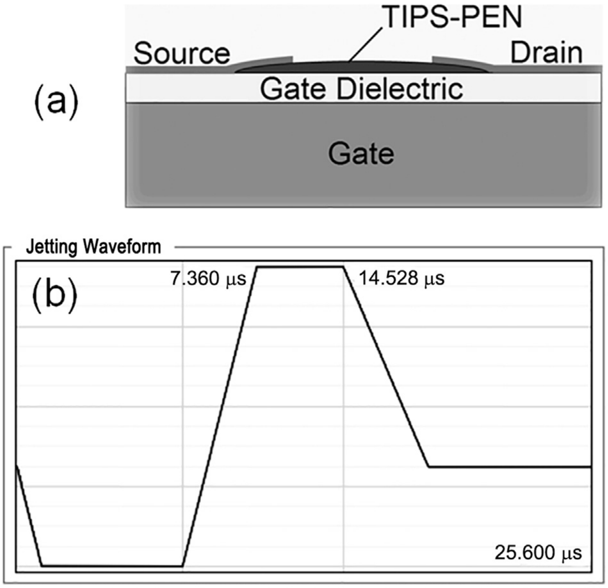

Fig. 1. (a) Schematic diagram of a bottom-gate/top-contact OTFT with an inkjet-printed TIPS-PEN as the channel semiconductor and (b) the 3-segment jetting waveform developed for stable jetting.

2-Phenylethyltrichlorosilane (PETS) is used as the organosilane molecule for SAM treatment. Prior to the surface treatment, the wafer has been cleaned in a piranha solution (70 vol.% H_2SO_4 + 30 vol.% H_2O_2) for 40 min at 90 °C and rinsed with copious amounts of deionized water. The sample is then soaked for 20 min in a 10 mM PETS solution in anhydrous toluene. In the final step, the substrate is washed with toluene and ethanol in sequence and blown dry with nitrogen. The surface of the sample is hydrophobic with a total surface energy of 44.79 mNm^{-1} (Dispersion component: 39.05 mNm^{-1}, Polar component: 5.74 mNm^{-1}).

Another hydrophobic substrate is prepared by spin coating a second dielectric layer of poly-4-vinylphenol (PVP) on top of the SiO_2 substrate. Poly(melamine-coformaldehyde) methylated as a cross-linker was mixed with PVP at a weight ratio of 4:6 and dissolved in propylene glycol 1-monomethyl ether 2-acetate ($C_6H_{12}O_3$, PGMEA). The total concentration of the solution is 10%. The solution is spin-coated at a revolution rate of 4000 rpm, forming a cross-linked PVP of 130 nm thickness after 90 min of vacuum bake at 180 °C. The surface energy of the PVP(dispersion component: 38.81 mNm^{-1}, polar component: 8.63 mNm^{-1}) is very close to that of the PETS-SAM-treated SiO_2 substrate owing to the phenyl groups on the surfaces of both substrates. The overall capacitance of the PVP/SiO_2 dielectric stack is 8.5 $nFcm^{-2}$ as measured at 1 MHz.

3. Results

3.1. Inkjet printing of isolating dots

The diameter and size uniformity depends heavily on the physical interaction between the substrate and the droplet of the ink solution. The ink solution and the pure solvent used in this experiment had a surface energy lower than that of the untreated silicon dioxide substrate and the UV-ozone-treated samples. Therefore, complete wetting on these substrates is observed with the contact angle measurement