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Double-Shot Inkjet Printing of Organic Charge-Transfer Compounds

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1. Introduction

Binary molecular materials, or organic charge-transfer (CT) compounds, provide versatile electronic functionalities as a result of ground-state electron transfer between component donor and acceptor molecules [1]. Quite high room-temperature electrical conductivities, reaching around 10^3–10^4 S/cm, can be achieved with a variety of CT compounds, e.g. tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ). These materials are often called "synthetic metals", and their particular electronic properties have been major subjects of study in materials physics for more than 30 years. However, the application of these functional organic materials into the "plastic electronics" is highly restricted, chiefly because of poor processability as a result of their high crystallinity and low solubility. In contrast, the study of printable conducting materials has been hitherto focused on soluble materials, including conducting polymers [2,3], inorganic nanometal clusters [4], or metal precursors [5]. Nonetheless it has been argued that the solvent affinity of these soluble materials causes problems in subsequent fabrication processes: the resultant films are vulnerable to further printing processes [6,7] or require post-processing annealing [3,5].

Here we present a double-shot inkjet printing (DS-IJP) technique where we take advantage of a unique characteristic of the CT compounds that individual component donor and acceptor molecules generally show much higher solubility than do their complexes. We show that microscale intermixing on substrates of dense droplets of inks containing donors and acceptors results in the instantaneous formation of CT complexes that form high-quality synthetic metal films without post-processing annealing.

2. Experimental

We used a piezoelectric drop-on-demand IJP apparatus with double IJP heads (*Microjet*, Picojet 2000CW). From the head, a droplet with volume of about 100 pL is ejected from an opening of ϕ50 μm and travels at a velocity v of 2–3 m/s. The solution was filtered through a mesh filter with a pore size of 0.5 μm before injection into the IJP heads. We prepared inks by dissolving donor molecules of TTF or tetraselenafulvalene (TSF), or acceptor molecules of TCNQ, 2-monofluoro-TCNQ (F_1TCNQ), or 2,5-difluoro-TCNQ (F_2TCNQ)] in dimethylsulfoxide (DMSO). A small amount of acetylcellulose (AC, average molecular weight 40,000) is added to the donor and acceptor inks.

In the fabrication of thin-film transistors (TFTs), we used n^+-silicon wafers as substrates with thermally grown silicon dioxide served as dielectric layers (500 nm, C = 6.7 nF/cm^2). Pentacene is used as the channel material. After it was purified by temperature-gradient sublimation in vacuum, thin films with 50-nm thickness were fabricated by thermal evaporation at 5×10^{-4} Pa on to substrate at 24 °C at a deposition rate of 0.05 nm/s with a vacuum chamber installed in an argon-filled glove box.

3. Results and discussions

Table 1 summarizes the solubility of some donors and acceptors and their CT complexes. This shows clearly that there is a considerable decrease in solubility as a result of complex formation in conventional CT complexes. In the DS-IJP process, **1)** a first drop of the donor ink is overprinted by **2)** a second drop of the acceptor ink at an identical position to **3)** form a mixed droplet on the substrate before **4)** the solvent is fully evaporated. In case of TTF-TCNQ, the reaction into CT complexes (step 3) occurs within 10 s, and evaporation of the solvent (step 4) almost finishes with additional 10 s at the substrate temperature of 35 °C. The conductivity of the TTF–TCNQ film is estimated to be 5–10 S/cm, which is close to the value for vacuum-deposited (VD) TTF–TCNQ films [8].

Fig. 1 shows optical microscope images of (a) DS-IJP TTF-TCNQ dot, (b) single-shot printed TTF dot, and (c) single-shot printed TCNQ dot, respectively. It is found that the DS-IJP films are composed of fine elongated plate-like crystals that densely aggregate on the substrates. In sharp contrast, single-shot printing of the molecular materials results in the formation of amorphous films (Fig. 1 (b)) or

Table 1 Solubility of organic molecules in DMSO

Donor	(g/L)	Acceptor	(g/L)	CT-Complex	(g/L)
TTF	770	TCNQ	16	TTF-TCNQ	0.8
		F_1TCNQ	110	TTF-F_1TCNQ	2
				TTF-F_2TCNQ	0.5
TSF	640	F_2TCNQ	20	TSF-F_1TCNQ	0.7
				TSF-F_2TCNQ	0.7

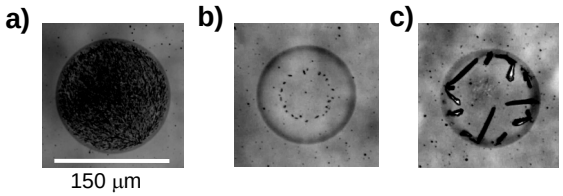

Fig. 1 Optical microscope images of deposited films containing 30 wt% of AC. a) TTF-TCNQ film fabricated with DS-IJP technique. Deposition of b) donor (TTF) or c) acceptor (TCNQ) ink without mixing each other. Same scales for all images.

much larger block-type crystals which were sparsely dispersed and isolated on the substrates. It is clear from this that the rapid formation and precipitation of the fine CT complex crystals in the deposited droplets is extremely effective for the fabrication of uniform and highly-conductive CT complex films.

Pentacene TFTs were fabricated by using the DS-IJP TTF–TCNQ films as the bottom-contact (BC) source/drain electrodes. The channel length was 200 μm and the channel width was 1000 μm. The transfer characteristics and the output characteristics of the device are shown in Figs. 2a and 2b, respectively. The field effect mobility was estimated to be 0.3 cm^2/Vs, the threshold gate voltage (V_{th}) was ~1 V, the turn-on voltage (V_{on}) was ~13 V, the on/off current ratio was 10^5, and subthreshold swing was 2 V/decade. The most noteworthy feature in the characteristics of the device with the DS-IJP thin film electrodes is the much narrower subthreshold region ($\Delta V = V_{th} - V_{on} \approx 10$ V) compared with the devices with vacuum-deposited TTF-TCNQ or Au electrodes ($\Delta V \approx 70$ V) [9]. Such a rapid rise in the transfer characteristics of the device with DS-IJP electrodes should be quite advantageous for low-voltage operations with both a low gate leakage and a high on/off drain current ratio.

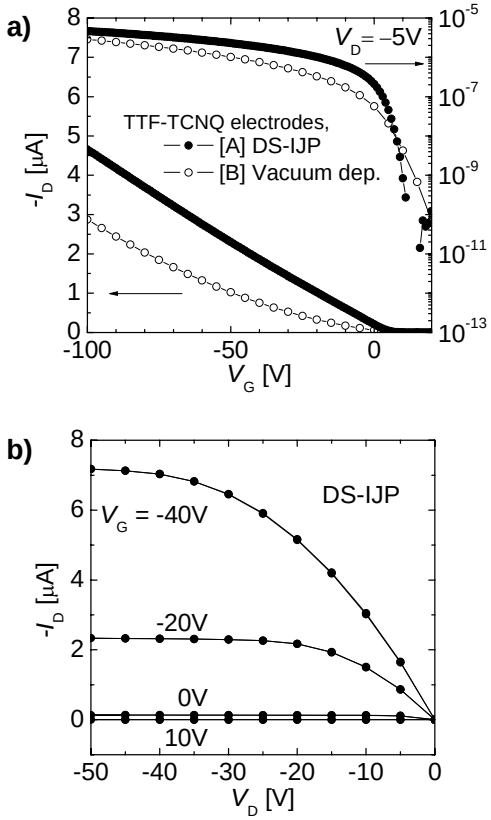

Fig. 2 a) Transfer characteristics of pentacene TFTs with source-drain electrodes composed of [A] DS-IJP and [B] vacuum-deposited TTF–TCNQ. b) Output characteristics of the device with DS-IJP TTF–TCNQ electrodes.

4. Conclusions

We successfully produced high-quality thin films of metallic CT complexes by a double-shot IJP technique that utilizes micro-liquid complex formation processes on the substrates. The method should be effective and applicable to a variety of metallic CT complex compounds. Source/drain contacts produced from the inkjet printed TTF-TCNQ films afforded high-performance pentacene TFTs that showed sharp on/off switching at low gate voltages.

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