Solution-based hybrid printing process for tiny channel length of organic transistors

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Abstract

Inkjet printing technique has been studying intensively on organic electronics, but its resolution is limited to about 20 to 50 μm due to the nozzle size and the interaction between the ink and substrates. In order to reduce the patterning feature of IJP, we use the contact printing as an auxiliary process to pre-define the desired deposition pattern. By use of the wetting and the de-wetting surface properties, the inkjet printed ink will self-align to the wetting surface to afford tiny feature. In this paper, Poly[3,4-(ethylenedioxy)thiophene] (PEDOT) was selected and patterned as electrodes of organic transistors. Octadecyltrichlorosilane (OTS) thin layer was used as the surface modifier. The minimum channel length can achieve to about 5 μm or so. The field-effect mobility of 0.001 cm^2/V-s and on/off current ratios of 10^3 were obtained in the ploy(3-hexylthiophene) organic thin film transistors fabricated by this proposed process.

Introduction

The application of solution-based direct-printing techniques to the deposition and direct-write patterning of functional materials is providing new opportunities for the manufacture of electronic devices, such as organic thin-film transistors (OTFTs) for applications in low-cost, large-area electronics on flexible substrates.[1–3] OTFTs fabricated with nonphotolithographic techniques such as ink-jet printing and micro-contact printing (μCP) have been proposed.[4,5] However, the ability of ink-jet printing technique to define micrometer-size patterns is limited to typically 20 to 50 μm due to the difficulties of controlling the flow and spread of liquid inks on surfaces. This is not sufficient for defining source-drain electrodes of OTFTs. Used 5 to 10 μm of channel lengths are required to achieve adequate drive current and switching speed. One approach to overcome these resolution limitations is to deposit the functional ink onto a substrate containing a predefined surface-energy pattern that control the flow and spreading of jetted droplets into place. This concept has been used successfully for patterning source–drain electrodes of polymer FETs with channel lengths of 5 μm by inkjet printing.[6] The performance of OTFTs would greatly benefit from further reduction of channel length to micrometer dimensions.

However, to achieve this, a detailed understanding of the various factors that govern the interaction of droplets containing a solute of functional material with a patterned surface is required. μCP has been applied mainly to the patterning of self-assembled monolayers (SAMs) for directly obtaining micropatterns below 10 μm.[7]

In this letter, we report that use of μCP and ink-jet printing hybrid technique to pattern and deposite source and drain electrodes of PEDOT on SiO_2 surfaces. The dewetting of the water-based conducting polymer inks on octadecyltrichlorosilane (OTS) patterned SiO_2 surface by μCP method was investigated. The pre-defined hydrophilic and hydrophobic area can confine the spreading of water based ink droplets of ink jet printing on desired hydrophilic areas to be source/drain electrodes with a small channel. This combined process can be used on area patterning instead of spin-coating whole area in conventional μCP patterning.

Treatment and Fabrication Processes

The OTFTs were fabricated with the bottom-gate (BG) and bottom-contact (BC) configuration. The fabrication processes of OTFTs are illustrated in Figure 1.

The photo resist was spin-coated on a silicon wafer with 4 μm film thickness and then developed by 2.5% TMAH [Figure 1(a)]. Stamps used in μCP were made of poly (dimethylsiloxane) (PDMS) and replicated from the silicon mold [Figure 1(b) & (c)]. The poly(dimethylsiloxane) (PDMS) elastomer (SylgardTM 184) was obtain from Dow Corning. The ink used for the present work was a freshly prepared 5 mM solution of OTS purchased from Aldrich using dehydrated hexane as the solvent. A paper tissue was wetted with OTS in a small petri dish, the stamp was saturated with ink by contact with the paper. After about 30 s the stamp was separated from the paper and the excess of OTS was allowed to evaporate during 3–5 min. This inking procedure was carried out under N_2 atmosphere [Figure 1(d)].

The UV-ozone treatment provided high wettability on heavily doped n-type silicon substrate as a common gate electrode and a thermally grown silicon dioxide film of thickness 300 nm served as the gate dielectric [Figure 1(e)]. The hydrophobic region was defined by μCP of OTS on the Silicon substrate [Figure 1(f)]. The source and drain electrodes were inkjet printed onto the hydrophilic region of the SiO_2 dielectric layer as the source and drain electrodes [Figure 1(g)]. The ink jet 3G platform, developed by ITRI[8] and equipped with Dimatix SX-3 piezoelectric print heads, was used for discharging the poly(3,4-ethylene-dioxythiophene): polystyrenesulfonate (PEDOT: PSS) (PH500) purchased from Baytron. The semiconducting conjugated polymer of P3HT was coated on the silicon substrate sequentially to complete the OTFT fabrication [Figure 1(h)]. The channel length (L) and width (W) were 5 and 1000 μm, respectively. The capacitance per unit area of the SiO_2 insulating layer is 10 nF/cm^2.

The current–voltage (I–V) characteristics of OTFTs were measured in N_2 by Keithley semiconductor analyzer (4200-SCS). For inspection, an optical-interferometry surface profiler is used to measure the thin film profile (SNU Presision Co.).

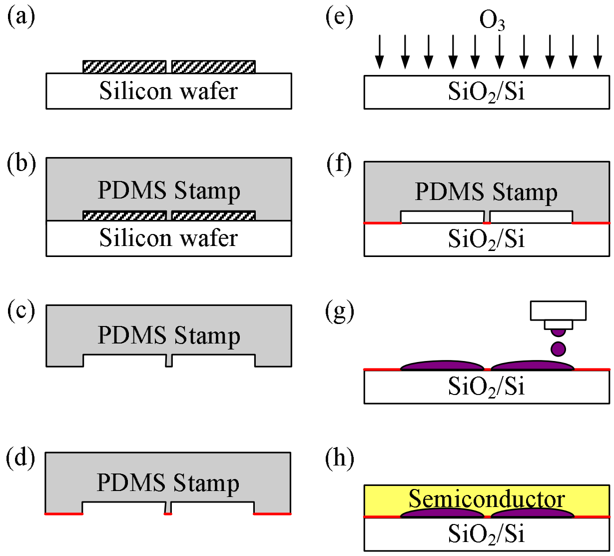


Fig. 1. Fabrication processes of Organic TFT using micro-contact printing and ink-jet printing.

Results and Discussion

We investigated the dewetting of the water-based conducting polymer PEDOT inks on patterned SiO_2 surfaces modified with the OTS. The surface tension of the water-based PEDOT is 59.5 dynes/cm at 25°C. To prepare the SiO_2/Si substrate with different wetting ability, the SiO_2/Si substrates were dipped into OTS and underwent UV-ozone treatment. The surface energy of SiO_2/Si substrate increases after UV-ozone treatment. The contact angle (CA) of PEDOT reduces to less than 5, which means the glass substrates become more hydrophilic. The thin film of OTS changes the wettability of a hydroxyl-terminated surface from hydrophilic to hydrophobic.

Figure 2 shows side views of the CA of PEDOT on UV ozone-treated SiO_2 layer (a) before and (b) after OTS treatment. The contact angle of the OTS-treated SiO_2 layer is higher than that of the UV ozone-treated SiO_2 layer. The difference is about 90˚, as shown in the figure. The SiO_2 layer treated with OTS clearly demonstrate their dewetting ability with respect to PEDOT, indicating that selective depositing of PEDOT is possible by ink jet printing.

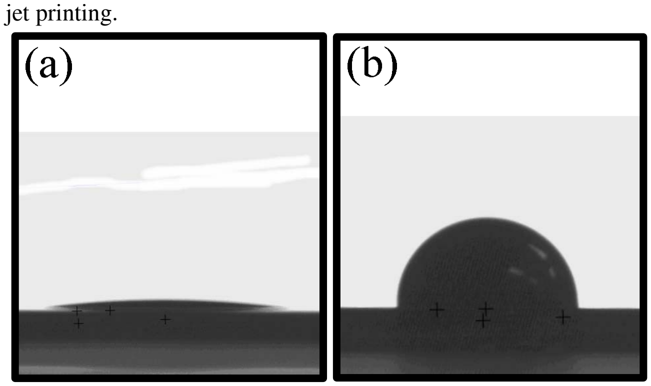


Fig. 2. (a) Contact angle of PEDOT on SiO_2 layer with UV-ozone treatment and (b) after OTS treatment.

There are three important factors governing the jetting behavior of piezoelectric print heads, i.e. pulse waveform, pulse frequency and driving voltage. The jetting behavior can be observed by a strobe capturing system integrated in the platform to evaluate the PEDOT solution. The break-off behavior of the PEDOT ink is captured from 35 to 60 micro-second (time interval: 5 micro-second) and shown in Figure 3(a). With a standoff of 1 mm, we have successfully modulated the ink-jet printing parameters on Spectra SX-3 for PEDOT ink, and therefore uniform PEDOT films are obtained on a UV ozone-treated SiO_2 layer.

The use of a highly hydrophilic region is important for well splitting conducting polymer ink droplets into source–drain electrodes of FET devices. The ozone process is not only to promote the interaction of OTS and SiO2, but it is also to have areas with dramatically different surface energy. Figure 3(b) shows the resulting pattern of PEDOT droplets landing on the top of a 5µm wide area with OTS SAM. This implies that after dewetting from the OTS, the contact line of the liquid PEDOT droplets move away from the OTS area and pins at the boundary of hydrophilic and hydrophobic areas. The edge of the resulting PEDOT pattern is very smooth and totally consistent to the µCP OTS pattern. This indicates that well defined fine feature pattern can also be achieved by this proposed hybrid process of µCP and ink-jet printing instead of µCP solely which is not good for direct printing of functional material for many times. Besides, we can get different devices on a substrate without suffering the whole area un-patterned coverage of spin-coating material.

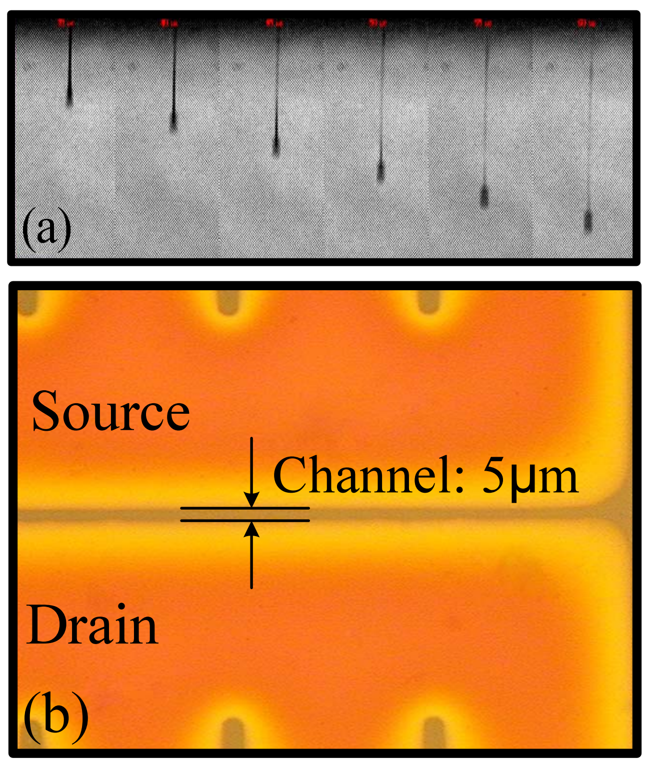
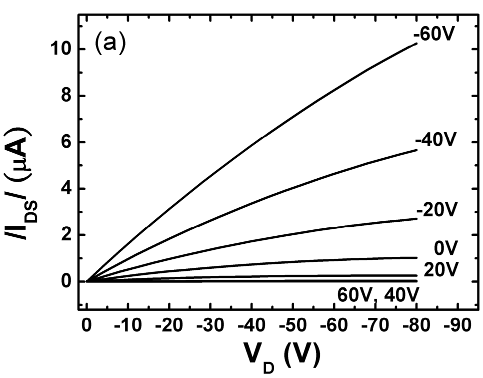


Fig.3. (a) Observation of drop break-off behavior from nozzle, (b) shows the pattern of dewetted PEDOT droplets split on top of a 5µm wide OTS layer .

Typical output curve characteristics of the P3HT OTFTs, using micro-contact printing and ink-jet printing, are shown in Figure 4(a). Good saturation behavior is obtained and only P-channel activity is observed for the device. With the increase of V_D, linear and saturation regions can be observed clearly in the plot. Strong field-effect modulation of the channel conductance was observed, with on/off current ratios (I_{on}/I_{off}) as high as 10^3. Figure 4(b) show characteristics of the transfer curve in the saturation region and the square root value of the current versus the gate voltage at source-drain voltage of -10V. The field-effect mobility (μ) and threshold voltage (V_T) were extracted from the measured transfer curve by comparing it with the standard transistor's current-voltage equation in the saturation regime: [9]

$$I_{DS,sat} = (WC_i/2L)\mu(V_G-V_T)^2$$

Where $I_{DS,sat}$ is the saturated drain current. The μ and the V_T of the OTFT were found to be 0.0016 cm^2/V-s and 34.5V, respectively. A maximum drain current of 10μA has been achieved for 5μm wide channel OTFTs. The drain currents of the OTFTs are improved due to extremely large W/L ratio (about 200). OTFT with a small channel length are attractive to increase drain current and speed due to less time for the carriers to cross the channel before recombination.



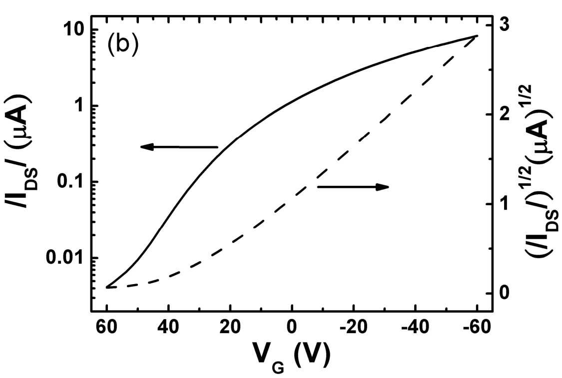


Fig.4. (a) Source-drain current-voltage characteristics of the OTFT using micro-contact printing and ink-jet printing hybrid technology; (b) typical transfer characteristics of the OTFT at a constant drain voltage of -60 V.

However, the threshold voltage shift is overwhelming. The interface between gate dielectric layer and organic semiconductor film mainly affects the value of threshold voltage. Threshold voltages of OTFTs often shift because of large amount of traps in this interface. These traps are attributed to improper morphology and impurity which will cause some defects on the interface. Figure 5 shows the profile of source/drain on the SiO_2 layer treated with OTS. The OTS still remains in the channel; however, its profile is very rough which corresponds to a large shift in threshold voltage. This indicates that smooth modified layer is important prior to spin coating the organic semiconductor.[10] So it needs to improve our process of OTS treatment, the defect issues can be mitigate for threshold voltage.

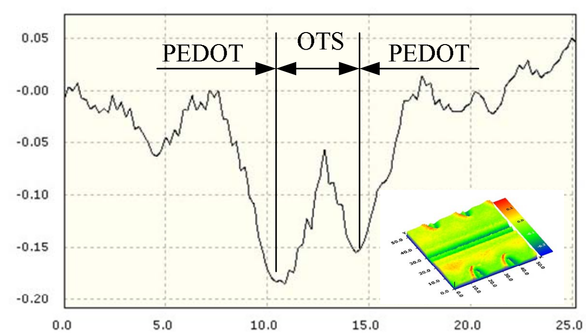


Fig.5. The profile of source/drain on the SiO_2 layer treated with OTS.

Conclusion

In conclusion, we developed a micro-contact printing and ink-jet printing hybrid technique to pattern OTFTs with 5 μm channel length. The bottom gate and bottom contact OTFTs demonstrate excellent electrical characteristics. Field-effect mobility and the on/off current ratio in the saturation regime as large as 0.0016 cm^2/Vs and on the order of 10^3 were obtained. This proposed non-photolithography technique is very suitable for patterning on a flexible substrate, and it can be potentially developed as a roll to roll patterning technique in the future.

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