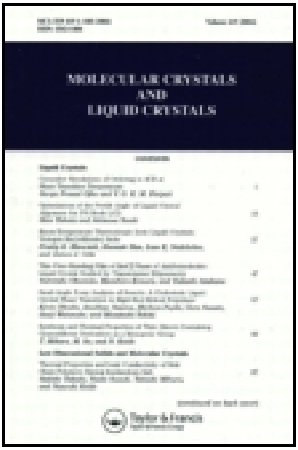

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Fabrication of Organic Thin-Film Transistors with Roll-Printed Electrodes Using Patterned Polymer Stamp

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The roll-printed electrodes of organic thin-film transistors (OTFTs) were fabricated by gravure or flexography printing using patterned poly(dimethylsiloxane) (PDMS) stamp with various channel lengths and low-resistance silver (Ag) paste on plastic substrates. The roll-printed OTFTs used poly(vinyl)(phenol) polymeric dielectrics and bis(triisopropyl-silylethynyl) pentacene organic semiconductors. The roll-printed OTFTs obtained had a field-effect mobility 0.08 ($\pm$0.02) cm^2/Vs, an on/off off current ratio of 10^4 and a subthreshold slope of 2.53 V/decade. The roll printing using patterned PDMS stamp for Ag paste transferring made it possible to fabricate a printed OTFT with a channel length as small as to 12 μm on plastic substrate.

Keywords: Ag paste; organic thin-film transistors; PDMS stamp; printed OTFT; roll printing

INTRODUCTION

Solution or liquid-based printing techniques have been used in the graphic art printing industry for more than 500 years to replicate information on paper in high volumes and at very low cost. The development of functional materials with well defined structural, chemical, physical, or biological functionality that can be processed from solution or liquid phase has inspired many research groups to explore the potential of

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adapting graphic art printing techniques to the manufacture of functional devices and structures [1]. The vision of many of these approaches is to integrate advanced functionality other than graphic information on to large-area substrates, for example flexible paper, plastic or large-area rigid glass, and be able to do this at a manufacturing cost that is much lower than could be achieved with more conventional manufacturing techniques [2]. Consequently, more recently, a variety of device fabrication techniques and processes including microcontact printing, inkjet printing, gravure printing, offset printing, and screen printing have been introduced for the fabrication of printed OTFTs, flexible displays, low-cost printed electronics, and printed electro-mechanical systems (PEMS) that aim specifically at reducing the fabrication cost [3–5].

Since the early 2000 s, scientists and engineers have succeeded in applying printing-related techno1ogies to create low-resolution organic electronics devices with micron-sized features [6].

The graphic arts printing equipment and printing processes must also be improved and adapted to meet the rather strict design rules for electronic circuits. Typical resolution capability of standard offset, gravure, screen, or inkjet printing is of the order of $50\sim100\,\mu m$. Clearly, these are not necessarily fundamental limitations. This field of application requires pattern and overlay accuracies down to $20\,\mu m$ for high-quality reproduction. In particular, roll printing is the collective name for traditional printing, which has been developed as alternative to conventional methods and as fabrication technology for microfabrication [7,8].

In this paper, we report in more detail a related study in which a roll printed OTFT was used for the fabrication of printed electrodes and soluble organic semiconductors on various plastic substrates. Gate, source, and drain electrodes of roll printed OTFT were fabricated by a high-resolution printing technique based on transferring a pattern from a patterned poly(dimethylsiloxane) (PDMS) stamp to a plastic substrate by physical contact using high-conductivity Ag paste. A roll printed OTFT with a poly(vinyl)(phenol) (PVP) as polymeric dielectric layer was formed using a spin-coating [9–11], and a bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) as an organic semiconductor layer was used in the ink-jet printing [12–14]. This is an attempt to enhance the accuracy of traditional printing to a precision comparable with optical photolithography, creating a low-cost, large-area, and high-resolution patterning process.

FABRICATION OF ROLL PRINTED OTFT

To fabricate a high-resolution and large-area printed OTFT, the following steps were performed: the design and manufacture of a engrave plate, the fabrication of a PDMS stamp, and a roll printing process. We used poly(ethylene naphthalate) (PEN), poly(ethylene terephthalate) (PET; Teijin Dupont Films), or polycarbonate (PC; i-Component) plastic substrates with thicknesses of 188, 200, and 200 μm and surface roughnesses of below 0.6, 11, and 2 nm, respectively. The I-010 (InkTec) and D-1502 (Daejoo) as conductive Ag paste with a low viscosity, below 1 kcps (at 22°C), a low density, below 1.08 cm^3, and a low resistance, below 0.084 Ω (sq/mil (25 μm)) were used for the fabrication of electrodes. PVP was used as organic dielectric layer. The dielectric strength of PVP is 5600 (DC volts/mil), sheet resistance is 10^{14} (Ω, 23°C, 50%), and dielectric constant is 3.3 (60 KHz). One of the solution-processable organic semiconductors used for the printed OTFT was TIPS-pentacene, which shows the highest reported field-effect mobility.

In this work, we fabricated master patterns by electron-beam lithography onto a quartz substrate. The channel lengths (L) of the unit elements were split between 10 and 80 μm, and line width (W) between 200 μm and 2 mm on the engraved plate with the pattern designed for 40 elements of different channel lengths and line widths to be placed.

The s-PDMS stamp was fabricated by mixing Sylgard 184A (silicone elastomer base) with Sylgard 184B (silicone elastomer curing agent) at a ratio of 10:1. It was poured onto the mask and air bubbles were removed by a vacuum pump. It was cured in a thermal dryer at 80°C for 1 hour. Then, the composite stamp was carefully peeled off from the master surface.

Figures 1 and 2 show the schematic fabrication process of roll-printed OTFTs by gravure or flexography printing using patterned PDMS stamp with various channel lengths and line widths, and with low-resistance Ag paste. The electrodes of roll-printed OTFT were fabricated by changing the print heads with patterned PDMS stamp using both gravure and flexography printings. As shown in Figure 1, the roll-printed electrodes were manufactured using gravure printing by the following process: a flexible plastic substrate, whose surface was hydrophilic and treated with plasma, was mounted on a flat plate; Ag paste was then poured into the patterned PDMS stamp surface; the paste was inked into the patterned PDMS stamp using a doctor blade; finally, the gate electrode was formed by forwarding and rotating the rubber roller wrapped patterned PDMS stamp. A polymeric dielectric of 10 wt% PVP having a thickness between 4000 and 7000 Å was formed on the fabricated gate electrodes using spin coating; it was then cured at 80°C for 10 min. The rubber roller was replaced with a source and drain electrode patterned PDMS stamp. The substrate formed with the gate electrode and polymeric dielectric layer was then

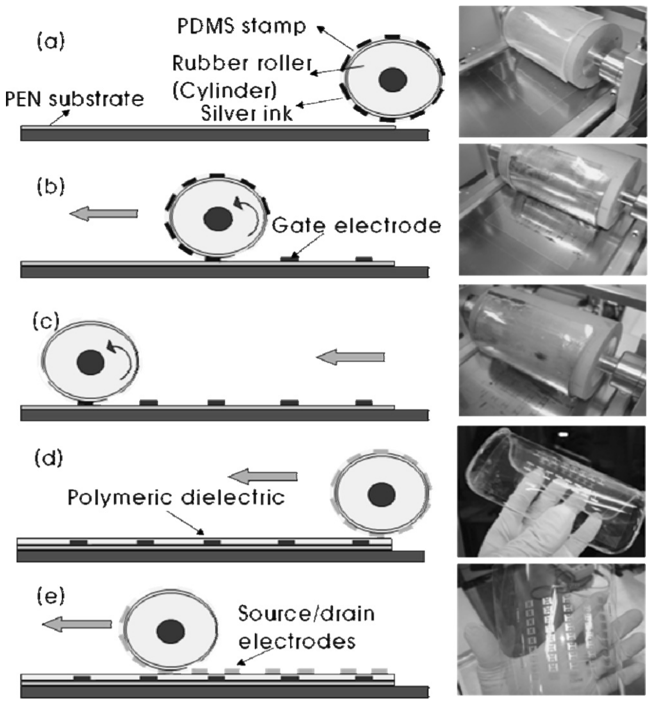


FIGURE 1 Fabrication of roll-printed OTFTs using gravure printing: (a) plastic substrate mounted on plate and inked Ag paste onto patterned PDMS stamp, (b), (c) roll-printed gate electrodes on plastic substrate, (d) spin-coated polymeric dielectric, and (e) roll-printed source and drain electrodes on plastic substrate.

mounted on the flat plate again. We fabricated source and drain electrodes using the patterned PDMS stamp of dimensions of $150 \times 150 \times 3$ (± 0.5) mm^3 between 10 and 80 μm channel lengths and differing channel widths and pattern shapes, and then it was replaced on roller wrapped PDMS stamp physically. The source and drain electrodes were formed by inking Ag paste onto the patterned PDMS stamp, doctor blading, and then roll printing. Finally, to form the organic semiconductor layer on the fabricated contact electrodes, we used ink-jet printing from a 1 wt% solution of TIPS-pentacene in chlorobenzene. The thin-films were formed by annealing at 60°C for 5 min in air.

Figure 2 shows the fabricating process of the printed OTFTs using flexography printing, where the pattern is transferred by contact printing to the sub roller with wrapping a plastic substrate from the

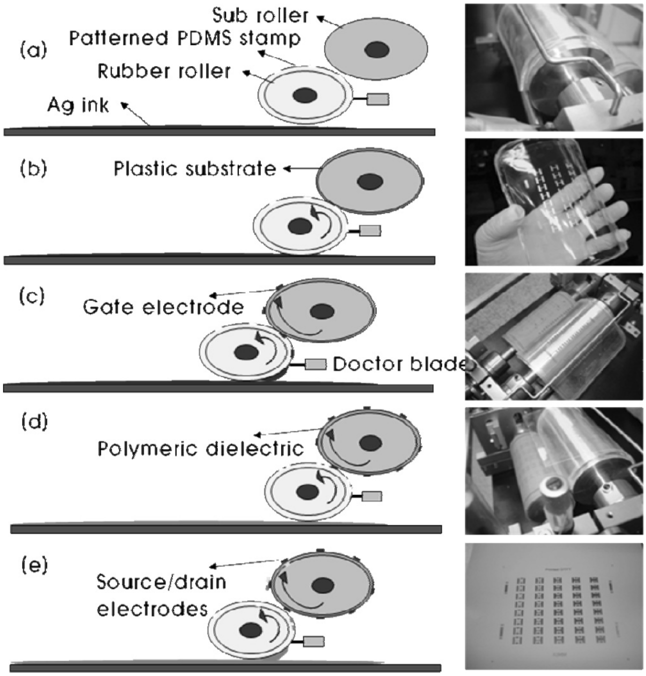


FIGURE 2 Fabrication of roll-printed OTFTs using gravure-offset printing: (a) pure and spread Ag paste onto plate (b) inking on patterned PDMS stamp using doctor blade, (c) roll-printed gate electrodes, (d) spin-coated polymeric dielectric, and (e) roll-printed source and drain electrodes onto preformed polymeric dielectric layer.

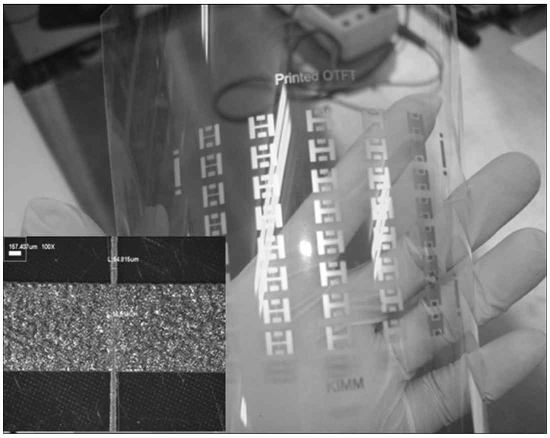
rubber roller with patterned PDMS stamp. The conditions for forming the electrode are a doctoring speed of 16 m/min and a patterning speed of 24 m/min. The roll-printed OTFT was fabricated using the same method as the gravure printing process.

EXPERIMENTAL AND RESULTS

By the above procedure, which included gravure and flexography printing using a high-resolution patterned PDMS stamp and two types of low-resistance Ag paste, a roll-printed OTFT with channel lengths between 12.6 and 76.7 μm were fabricated on $150 \times 150\,\mathrm{mm}^2$ plastic substrate without pattern defects.

Figures 3(a) and 3(b) show the respective actual rubber roller wrapped patterned PDMS stamp and the roll-printed OTFT devices with various channel lengths between 12.6 (13.4) and 76.7 (72.1) μm,

(a)



(b)

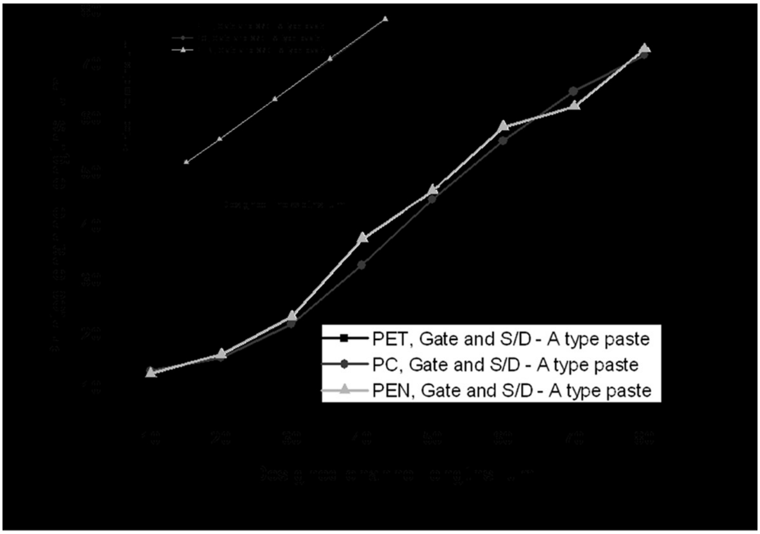
FIGURE 3 Images of fabrication of printed OTFT: (a) PDMS stamp with channel lengths between 10 and 80 μm and (b) roll-printed TIPS-pentacene OTFTs on the $150 \times 150\,mm^2$ PEN plastic substrates. (Array type patterned PDMS stamp (a) and channel length of 13 μm (b) are shown in the inset.).

with various channel widths and spaces between patterns. Figure 3(a) shows that the patterned PDMS stamp has a replicated pattern exactly corresponding to the master pattern and has a high accuracy of filling and releasing. Also, as a surface characteristic, by measuring the wettability, it was demonstrated that the patterned PDMS stamp was hydrophobic with a contact angle of 110°, and a surface energy of 22 dyne/cm. The adhesion force was 12 nN, which was very low.

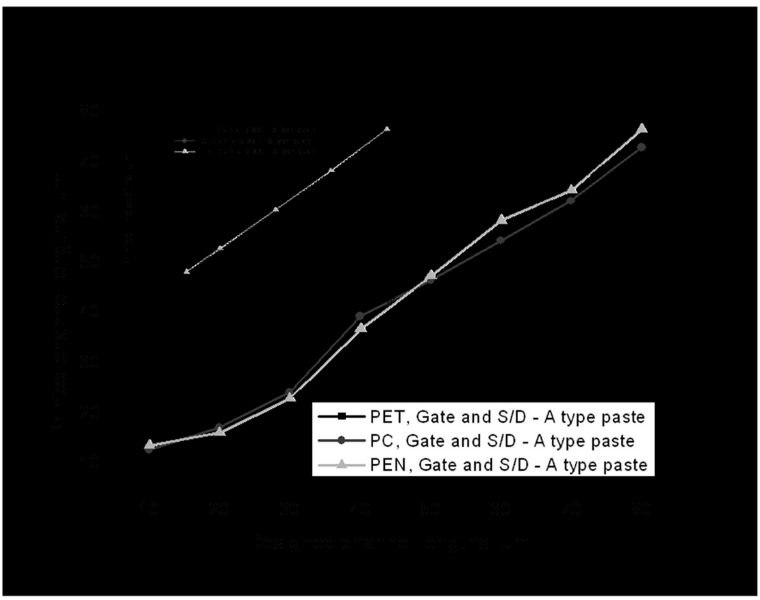
Figure 3(a) shows the result for a patterned PDMS stamp, and it was divided into 4 areas with a unit device, a 4-pixel, and a 6-pixel array structure (see the inset). Figure 3(b) shows an image of a printed OTFT array using TIPS-pentacene as the semiconductor, PVP as the gate dielectric layer, and Ag paste gate, source and drain electrodes.

The pattern transfer experiments were performed using DG-1502 or TEC-I010 as roll printing Ag paste; these pastes were applied onto a surface treated plastic substrate using the rubber roller. With regard to the electrical characteristics, measurements of the conductivity, confirmed that the roll-printed electrode had a higher conductivity with sheet resistances of $0.052\,\Omega/\square{\sim}0.0211\,\Omega/\square$ and line resistances of $0.6\,\Omega/\square{\sim}0.3\,\Omega/\mathrm{cm}$, which was very low. The surface properties were also enhanced, as confirmed by measurement of the surface roughness, which changed from ${\sim}1.5\,\mu\mathrm{m}$ to less than 800 nm (not shown here). The measurements revealed that the surface properties and enhances their performance of roll-printed OTFTs, such as roughness, sheet resistance, line resistance, and density, were improved.

Figure 4 shows a graph of the measurement results of variation characteristics including the designed channel lengths versus the printed channel lengths plot for roll-printed OTFTs. Figures 4(a) and 4(b) show the respective results of the variation between the reproducibility of printed patterns obtained by gravure and flexography printings; these results were obtained by analyzing cases in which systems have both line widths and channel lengths. Figure 4(a) shows the gravure-printed OTFTs with channel lengths between 12.6 and 76.7 μm (designed $L = 10$ to 80 μm) and channel widths between 204.3 and 1965.6 μm (designed $W = 200$ to 2000 μm). Figure 4(b) shows to flexography-printed OTFTs with channel lengths between 13.4 to 72.1 μm and channel widths between 211.2 to 1995.2 μm for Ag source and drain contact electrodes on various gate electrode patterns. Figure 4(b) also shows that the roll-printed electrodes have a transferred pattern exactly corresponding to the engraved plate and they have a higher accuracy of transferring onto plastic substrate as compared to the electrodes shown Figure 4(a). The roll-printed electrodes were showed high fidelity and good reproducibility above 40 μm. The channel length deviations for 40 to 80 μm patterns were less than −10%. However, the channel lengths for 10 to 30 μm patterns increased by −20 to −30% owing to Ag paste diffusion and the shrinkage, which occurred during transferring, printing, and curing between the Ag paste electrode and polymeric dielectric layer or plastic substrate interface. As compared with that in Figure 4(a), the distribution of channel length variation within each pattern in Figure 4(b) is a little bit different, which known to be due to the ink transfer mechanism,



(a)



(b)

FIGURE 4 Variations in characteristics of designed line widths versus printed line widths for source and drain electrodes of (a) gravure- and (b) flexography-printed OTFTs. (The variations in characteristics, i.e., designed line widths versus printed line widths for gate electrodes, are shown in the inset.)

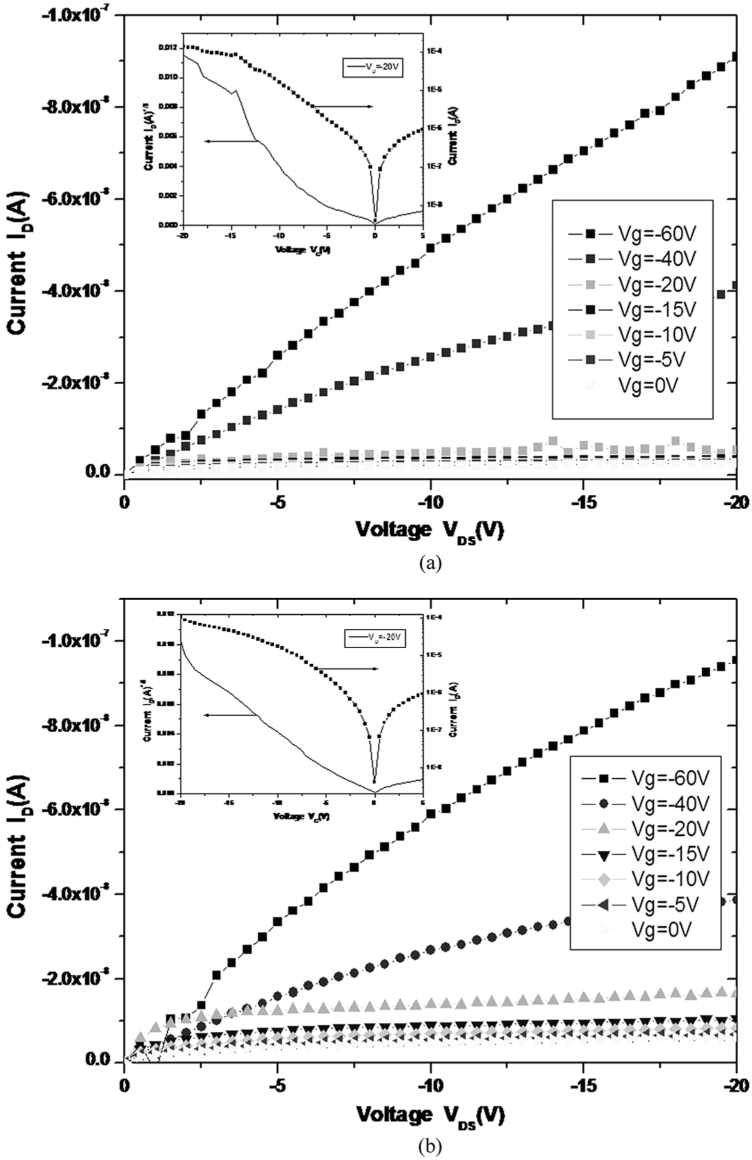


FIGURE 5 Drain current I_{DS} versus drain voltage V_{DS} output characteristics of roll-printed TIPS-pentacene OTFT ($W/L = 477\,\mu m/16\,\mu m$) with an Ag paste gate electrode, spin coated PVP dielectric, Ag paste source and drain electrodes on PEN substrate in the (a) gravure printing and (b) flexography printing. (The transfer characteristics of drain current I_{DS} versus gate voltage V_{GS} and $|I_{DS}|^{1/2}$ versus V_{GS} at $V_{DS} = -20\,V$ are shown in the inset.)

coefficient of thermal expansion (CTE), and surface roughness of the polymeric dielectrics used. Furthermore, it was established that the roll-printed OTFT was completely fabricated due to the effect of the contact between the Ag paste electrode and the plastic substrate and polymeric dielectric layer. In our proposed method, it is necessary to optimize the surface treatment process, accurately control the printing conditions, and the fabrication processes including curing temperature and the curing time.

Roll-printed OTFTs were fabricated by a near-room-temperature process and characterized in air. Figures 5(a) and 5(b) show the measurement results for the transfer and output characteristics, respectively. Figure 5(a) shows a typical plot of the output characteristics at various gate voltages V_{GS} for a drain current I_{DS} versus drain voltage V_{DS} plot, as well as from a graph of the transfer characteristics; these characteristics include an I_{DS} versus V_{GS} plot and an $|I_{DS}|^{1/2}$ versus V_{GS} plot (shown in the inset), and correspond to a roll-printed OTFT using gravure printing with a channel length $L = 16\,\mu m$ (designed $L = 20\,\mu m$) and a width $W = 477\,\mu m$ (designed $W = 500\,\mu m$), with 1 wt% TIPS-pentacene as the semiconductor, 5600 Å spin-casted PVP used as the gate dielectric, an Ag paste used as the gate, and source and drain electrodes. The field-effect mobility was $0.1\,cm^2/Vs$, while the threshold voltage was approximately $-3.54\,V$. The on/off current ratio was above 10^4 when V_{GS} was scanned from -20 to $+5\,V$. Figure 5(b), which corresponds to a roll-printed OTFT using flexography printing, as shown in Figure 5(a), shows a plot of the transfer characteristics, and the calculated field-effect mobility is $0.08\,cm^2/Vs$ at $V_{DS} = -18\,V$.

As a result of evaluating roll-printed OTFTs fabricated by the proposed processes using low-resistance Ag paste and a high-resolution engrave plate, the following parameters were obtained: field-effect mobility as large as 0.1 (± 0.02) cm^2/Vs, on/off current ratio of 10^4, a subthreshold slope of 2.53 V/decade, and a threshold voltage of $-3.54\,V$.

CONCLUSIONS

To fabricate a large-area roll-printed OTFT, we are developing a high-resolution roll printing technique based on transferring a pattern from patterned PDMS stamp to flexible plastic substrates by nanoparticle Ag inks gravure or flexography printing. The roll-printing using patterned PDMS stamp for Ag paste transfer patterning made it possible to fabricate printed OTFT with a channel length as small as $12\,\mu m$ on plastic substrates, which had been hardly patterning in the previous traditional printing techniques. The number of steps in the proposed fabrication process was reduced by 20 steps as compared to that in conventional fabrication techniques. This technology of using printed electrodes and soluble organic semiconductors combined with large-area printing techniques is believed to have the potential to reduce manufacturing costs is by eliminating the need for photolithography.

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