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Fabrication of 6,13-bis(triisopropylsilylethynyl)–pentacene thin-film transistors with the silver ink transfer method using a polymer stamp

Tae-Yeon Oh, Nam-Su Kang, Ki-Young Dong, Seongpil Chang, Jung-Ho Park, Shin-Woo Jung, Seung-Jun Lee, and Byeong-Kwon Ju

Display and Nanosystem Laboratory, School of Engineering, Korea University, Seoul 136-713, Republic of Korea

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* Corresponding author: e-mail bkju@korea.ac.kr, Phone: +82 (0)2 3290 3791, Fax: +82 (0)2 3290 3237

We fabricated 6,13-bis(triisopropylsilylethynyl)–pentacene (TIPS–pentacene) thin film transistors using a direct metal transfer method. Using different metals, such as Au and Ag ink, electrode patterns are formed from the relief region of the polymer mold. TIPS–pentacene TFTs using the Ag ink transfer method show a similar performance to those using the Au

metal transfer method. This method has advantages over the Au metal transfer method because it does not require vacuum equipment and a dry etching process. The self-assembled monolayer (SAM) treated device exhibits a carrier mobility of $9.5 \times 10^{-2} \text{ cm}^2/\text{V} \cdot \text{s}$, and an on/off ratio of 4.6×10^4 .

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1 Introduction Transfer printing techniques are very attractive for the fabrication of organic thin film transistors (OTFTs) used for such things as flexible displays, integrated circuits, and RFID tags [1, 2]. A key issue for these organic devices lies in the possibility to micropattern various kinds of metallic materials. To define these micropatterns, several patterning methods have been developed, such as micro contact printing (μCP), photolithography, imprint lithography [3], and ink-jet printing [4]. Among these methods, imprint lithography has several advantages, such as a low cost, easy processing, and nanometer scale resolutions. However, imprint lithography has difficulty in controlling the residual layer, which requires an additional reactive ion etching step to remove the residual layer, which may distort the patterns and damage the surface of the materials. μCP is a well-known and important method for selective patterning onto a surface with a variety of materials [5]. μCP , using an elastomeric stamp such as poly(dimethylsiloxane) (PDMS), is a rapid printing technique which is capable of patterning onto flexible substrates without a dry etching process, in contrast with imprint lithography. This method also shows fine edged

transfer patterns in contrast with inkjet printing. Generally, μCP is used to form self-assembled monolayer (SAM) patterns on the metal surfaces of substrates, such as Au and Ag, and then metal patterns are formed by selective wet etching [6]. Zaumseil et al. show a cross-bar type polymer non-volatile memory device using a direct metal transfer (DMT) method [7]. However, these techniques need an additional dry etching process or vacuum equipment to evaporate the metal. Therefore, we fabricated 6,13-bis(triisopropylsilylethynyl)–pentacene (TIPS–pentacene) thin-film transistors (TFTs) onto silicon dioxide (SiO_2) surfaces using a silver ink transfer method. The Ag ink transfer method is a rapid and cheap process because it does not use vacuum equipment in fabricating the electrodes, and is without a wet or dry etching process.

2 Experimental Figure 1 shows the μCP process for the electrode material using Au and Ag ink. First, the PDMS stamp surface was coated with a monolayer of a releasing material, octadecyltrichlorosilane (OTS), in order to detach the Au layer easily. After coating the stamp with OTS, a 200 nm thick Au layer was deposited on the PDMS

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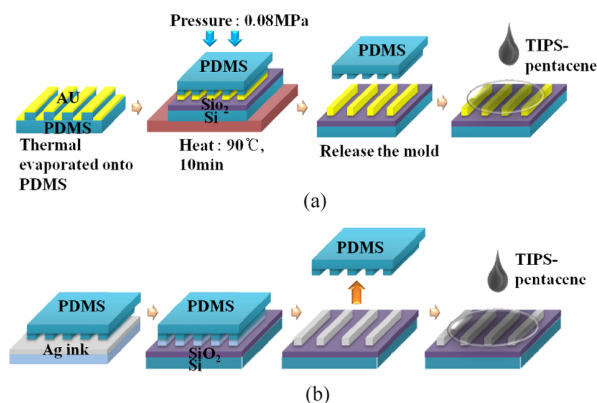


Figure 1 (online colour at: www.pss-rapid.com) The schematic diagram of micro-contact printing process: (a) Au electrodes transfer, (b) Ag electrodes transfer.

mold by a thermal evaporator at a rate of 2 \AA/s . To transfer the Au pattern, the Au-deposited PDMS stamp was placed on top of a $90 \text{ }^\circ\text{C}$ pre-heated SiO_2 substrate and a pressure of 0.1 MPa was applied by an imprinting equipment for 10 min to ensure that the contact region at the interface was as conformal as possible. When the PDMS stamp was released, the Au on the relief regions of the PDMS stamp was transferred onto the SiO_2 substrate, forming the finger type electrode pattern. In order to transfer the Ag ink (Ink tech.), Ag ink was spin-coated onto a substrate such as glass, then the PDMS stamp was attached on the Ag coated substrate without pressure. Few minutes later, the stamp was peeled off with an Ag ink layer left onto relief regions of the PDMS stamp. After that, the Ag coated stamp was attached onto the SiO_2 substrate for 5 min with weak pressure. After releasing the stamp, Ag ink layer covering the relief region of the stamp was transferred onto the SiO_2 substrate. The printed Ag ink pattern was cured at $150 \text{ }^\circ\text{C}$ on the hot plate for 10 min, finally Ag electrodes were formed. To improve the charge injection, the SAM was formed by immersing the Ag electrodes in an ethanolic solution of pentafluorothiophenol (PFTP). A $2 \text{ wt}\%$ TIPS–pentacene solution in an anisole solvent was deposited by a drop casting method as an active layer. The workfunction of the materials was measured by a Photoelectron Spectrometer (AC-2, RKI Instruments).

3 Results and discussion Figure 2(a) shows the optical image of the finger type Au electrode printed on the Si/SiO_2 substrate. The channel length of the transferred electrode is $100 \text{ }\mu\text{m}$. The transferred Au electrode surface was cracked since the elastomeric PDMS mold was deformed during the contact printing [8], thus the device performance was degraded. Figure 2(c) shows the image of the transferred Ag ink electrode. The image shows a fine edge pattern comparable to the transferred Au pattern. Figure 2(b) and (d) show optical images of the drop-casted TIPS–pentacene layer on the transferred Au and Ag pattern. The contact printing process depends on the differential adhesion between the two substrates [9]. It is known

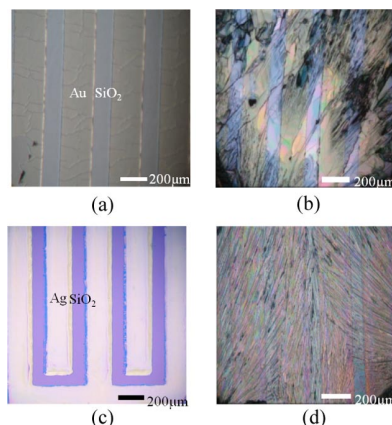


Figure 2 (online colour at: www.pss-rapid.com) Optical images of the electrodes on Si/SiO_2 substrate: (a) transferred Au, (b) TIPS–pentacene on the transferred Au, (c) transferred Ag ink, (d) TIPS–pentacene on the Ag ink.

that a PDMS mold (19.8 mJ/m^2) has a much lower surface energy than the SiO_2 substrate [10]. The Au deposited on the PDMS mold was transferred onto the SiO_2 substrate due to the differential surface adhesion. However, since Ag ink is a liquid at room temperature, the transferred Ag ink electrode does not show cracks. It needs a very weak pressure to transfer the Ag ink layer. The stamp of source–drain array contains about 50 microstructures: the yield of the transfer process is more than 98%. The output and transfer characteristics of TIPS–pentacene TFTs using the Au, Ag transfer method are shown in Fig. 3(a) and (b), respectively. The TIPS–pentacene TFT with transferred Au electrodes and Ag ink electrodes show a saturation mobility of $8 \times 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$ and $6.1 \times 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$, respectively. The mobility is similar to that of a device using the Au transfer method. The devices using the Ag ink have not shown good performances compared to the devices using the evaporated Au electrode. This may be mainly due to the limited carrier injection from the electrode to the semiconductor, especially in bottom-contact OTFTs where the effect of the barrier height from the metal to the semiconductor is known to be more pronounced than that of their top-contact equivalents due to the smaller contact area [11]. The device with a silver electrode shows a high threshold voltage since the workfunction of the silver ink electrode (4.6 eV) does not coincide with the highest occupied molecular orbital of the TIPS–pentacene (5.3 eV), so a hole injection barrier is formed at the silver electrode and semiconductor interface [12]. For an effective carrier injection into the organic layer or the metal electrode, the workfunction of the metal electrode has to match the lowest unoccupied molecular orbital (LUMO) of the organic molecules [13]. The electrical performance of the OTFT is strongly related to the ohmic contact for the organic/metal interfaces. Therefore, in order to match the energy level at the organic/metal interfaces, a SAM treatment was applied onto the silver electrodes. Some groups have reported that the SAM treatment can tune the metal workfunction [14,

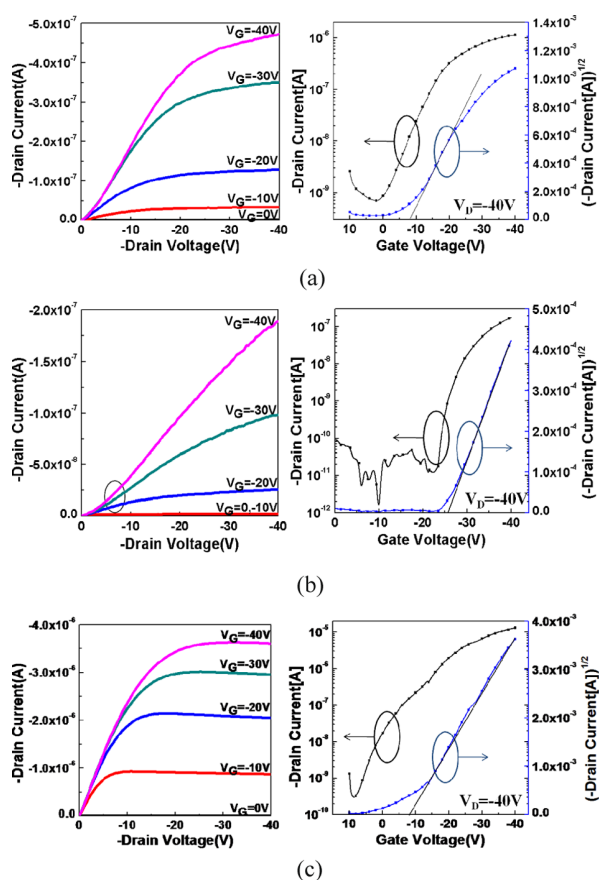


Figure 3 (online colour at: www.pss-rapid.com) Output and transfer characteristics of TIPS–pentacene TFT with various electrodes: (a) transferred Au, (b) transferred Ag, (c) transferred Ag-PFTP.

15]. The PFTP SAM treatment makes the workfunction of Ag increase from 4.7 eV to 5.35 eV, thus the PFTP treated Ag electrode is well matched to the TIPS–pentacene. The measured workfunction of the Ag ink electrode and the PFTP treated Ag ink electrode (from Sigma Aldrich) is 4.6 eV and 5.5 eV, respectively. The change of the workfunction by the PFTP SAM is due to the dipole moment of the molecule [16]. Figure 3(c) shows the electrical characteristics of the OTFT with the PFTP treated Ag electrodes. The mobility of the TIPS–pentacene TFT with the Ag-PFTP electrodes shows a higher mobility of $9.5 \times 10^{-2} \text{ cm}^2/\text{V} \cdot \text{s}$ than the device with the pristine Ag electrode. The on/off ratio is also improved. The threshold voltage of the Ag-PFTP device is lower than the pristine

Table 1 Electrical characteristics of TIPS–pentacene TFT with Au, Ag, Ag-PFTP electrodes.

parameters	Au	Ag	Ag-SAM
V_T (V)	-8.2	-25.7	-9
μ ($\text{cm}^2/\text{V} \cdot \text{s}$)	8×10^{-3}	6.1×10^{-3}	9.5×10^{-2}
on/off ratio	1.6×10^3	1.7×10^4	4.6×10^4
SS (V/decade)	2.88	3.47	2.43

Ag device. Since the threshold voltage is related to the interfacial trap density at the channel and gate dielectric interface, the TIPS–pentacene TFT treated with PFTP SAM has a less positive trap density [17]. Table 1 summarizes the electrical characteristics of the TIPS–pentacene TFTs with the Au, Ag ink and Ag ink-PFTP electrodes. The mobility of the OTFT with the SAM-treated Ag electrodes is comparable to that of the previously reported TIPS–pentacene TFT with evaporated Au electrodes [18].

4 Conclusion In summary, we fabricated TIPS–pentacene TFTs using the direct metal transfer method without a wet or a dry etching process. Of greatest importance is the fact that contact printing technology using Ag ink is a more rapid and cheap process than the one using Au metal because it does not require vacuum equipment. The performance of the OTFT fabricated by the Ag ink transfer method is similar to the one fabricated by the Au metal printing method. Since the silver ink device performance needs to be improved, the Ag ink electrode was treated with PFTP SAM. The TIPS–pentacene TFTs with the PFTP-Ag ink electrode show improved electrical characteristics, especially in the mobility which is increased by more than 10 times. Our silver transfer method using the polymer stamp can be used on flexible substrates as well as on rigid substrates because of its nonaqueous, low pressure, and low temperature process.

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