Thin Solid Films 554 (2014) 127–131

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Fabrication of polymer-based transistors with source–drain electrodes made of carbon nanotubes and silver nanoparticles by soft lithography techniques

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ARTICLE INFO

Available online 7 September 2013

Keywords:
Organic field effect transistor
Soft lithography
Poly(3-hexylthiophene)
Printed source–drain electrodes
Carbon nanotube
Silver nanoparticles

ABSTRACT

In this study, we have developed multilayer deposition and patterning processes with a resolution of 1 μm that can be used to fabricate all-printed, polymer-based organic field-effect transistors (p-OFETs) on the basis of vacuum-free, solution-processable soft lithography techniques. We have used regioregular poly(3-hexylthiophene) (P3HT) as a soluble polymer semiconductor and poly(methylmethacrylate) as soluble polymer gate insulators. We have compared the electrical properties of p-OFETs with multi-walled carbon nanotubes (MWNTs), silver nanoparticles (NPs), and their composites as printed source–drain (S–D) electrodes in order to fabricate vacuum-free, all-printed p-OFETs. The p-OFETs with MWNT S–D electrodes exhibited higher hole mobility and on/off ratios than the devices with Ag NP S–D electrodes owing to better contact at the MWNT/P3HT interface. The high sheet resistance of MWNT electrodes was considerably reduced by mixing with Ag NPs. Both the contact resistance and channel resistance were maintained at low values, resulting in improved electrical properties of p-OFETs.

1. Introduction

Solution-processable organic field-effect transistors (OFETs) have attracted increased interest as key components of printed and flexible electronics because of their suitability for the fabrication of economically friendly, flexible electronic circuits over large areas and at low temperatures. Typical examples of their application are in flexible radio-frequency identification tags, large-area readout circuits for sensing devices, flexible memory devices, and backplanes for high-resolution active-matrix displays [1–8]. There has been tremendous progress in conjugated organic semiconductors, especially those that provide field-effect mobilities, μ, above 1 cm^2V^{-1} s^{-1} [7–11].

Although the field-effect mobility for typical solution-processed conjugated polymers such as poly(3-hexylthiophene) (P3HT) has often been two or more orders of magnitude lower than that of crystalline conjugated small molecules, they are advantageous for depositing uniform thin films using conventional printing techniques. The patterning and multilayer deposition of component materials such as electrodes, dielectric layers, and organic semiconductors, are becoming more important for practical applications.

Photolithography and nanoimprinting lithography techniques are advantageous for high-resolution manufacturing but are cost-ineffective and time-consuming. Furthermore, they require a subtractive process to remove unwanted materials, such as developing and etching. The nanoimprinting of metal and inorganic materials requires high temperature and pressure. Therefore, they limit the variation of materials and device structures owing to the requirement of stable materials for those processes [12–15]. Therefore, the establishment of alternative, low-temperature, damage-free multilayer deposition and patterning processes suitable for soluble organic materials is one of the most important emergent issues for the application of organic electronic devices.

Soft lithography techniques are additive-type high-resolution printing methods with a typical resolution of less than 100 nm and are a cost-effective alternative to photolithography. There are various soft lithography techniques such as micro-contact printing [16,17], microtransfer molding [18], solvent-assisted micro-contact molding [19], replica molding [20], micro molding in capillaries [21,22], and nanotransfer printing (nTP). In particular, nTP involves the pattern transfer of a dried film from a silicone elastomer such as polydimethylsiloxane (PDMS) at low pressure and temperature that is capable of damage-free direct patterning and direct printing of functional films onto soluble organic materials [23–26].

In this study, we have developed a direct multilayer deposition and patterning process for soluble polymer films and electrode materials and fabricated polymer-based all-printed OFETs (p-OFETs) on the basis of soft lithography techniques. Here, we used an nTP process in order to achieve the fabrication of damage-free, multilayer deposition of soluble polymers such as poly(methylmethacrylate) (PMMA) and P3HT. We have used P3HT as a polymer semiconductor and PMMA as a soluble gate insulator. We chose multi-walled carbon nanotubes (MWNTs), silver nanoparticles (NPs), and their composites as the

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0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2013.08.107

printed source–drain (S–D) electrode materials for fabricating vacuum-free, all-printed p-OFETs at temperatures below 150 °C.

2. Experimental details

We prepared the bottom gate–top contact and bottom gate–bottom contact p-OFET arrays as shown in Fig. 1. An indium-tin-oxide (ITO)-coated glass substrate was mainly used as the substrate. First, ITO was pre-patterned by conventional photolithography and an acid treatment, followed by the removal of the resist film and rinsing with deionized pure water [Fig. 1(a)]. Second, PMMA (Aldrich) films were formed by dip-coating a chloroform solution (50 g/l) on a patterned PDMS (Shin-Etsu Chemical SIM-260 or 240) stamp with a typical depth of 10 μm. PMMA on the raised area of the PDMS stamp was then transferred onto the substrate twice at 150 °C for the first deposition and 100 °C for the second deposition at a typical pressure of approximately 1 MPa in air [Fig. 1(b)]. The typical thickness of PMMA was approximately 1 μm with an average molecular weight of 996,000. The capacitance per unit area, C_i, of the PMMA gate insulator was approximately 3.5 nF/cm^2. Thirdly, the dip-coated P3HT (Luminescence Technology Corp.) film on PDMS from a chloroform solution (5 g/l) was selectively transferred to the raised area of the patterned silicon or resist film (selective lift off) to fabricate the top contact device. After that, the PDMS stamp was placed in contact with the substrate in order to transfer the patterned P3HT film in a nitrogen atmosphere at a temperature range of 30–100 °C and a pressure of 1–2 MPa [see Fig. 1(c) and (d)].

MWNT and Ag NP inks dispersed in alcohol-based solvents were spin- or dip-coated on a patterned PDMS stamp. Here, the average diameter and the length of the MWNTs were approximately 10 nm and 800–1000 nm, respectively. The MWNT and Ag NP inks were supplied from Sumita Nanotechnologies in collaboration with Daido Chemical Coating and DIC Corp., respectively. After depositing MWNTs, the dried stamp was soaked in alcohol for 1 min in order to remove the surfactant materials surrounding the mesh-like MWNT films. Ag NP ink was then spin-coated on the MWNT-coated PDMS stamp [Fig. 1(e)] and permeated into the mesh-like MWNT network. After that, the PDMS stamp was placed in contact with a substrate in order to transfer the patterned S–D electrodes. Finally, the samples with Ag and Ag-MWNT composite electrodes were heat-treated at 150 °C in a nitrogen atmosphere in order to prevent the oxidization of Ag and P3HT films [Fig. 1(f)]. The thickness of the MWNTs and Ag NP films were approximately 200 nm. The typical channel lengths in this study were 40, 80, 160, 240, and 320 μm, and the channel width was fixed at 2 mm.

The devices were then measured in a vacuum chamber ($<10^{-3}$ Pa) after evacuation for at least 1 h at 30 °C in order to avoid the instability in p-channel device operation of P3HT films because donor-type (p-type) materials with low ionization potential such as P3HT are easily doped with oxygen and become unstable in the presence of humidity [27,28]. The current-voltage characteristics of the FETs were measured using an electrometer (Keithley, Model 6517) and picoammeter (Keithley, Model 6487). The thickness and gate insulator capacitance were estimated from the capacitance curves measured by a precision LCR meter (Agilent Technology Model 4284A). The sheet resistances of the S–D electrode materials were estimated from the relationship between the resistances of 150–200-nm-thick, 500-μm-wide wired electrodes with lengths in the range of 1–10 mm. We fabricated 10 samples for each material. The sheet resistance obtained for 10 wired MWNTs, Ag, and Ag-MWNTs electrodes were 3000–5000, 0.5–0.8, and 0.2–0.3 Ω/square, respectively.

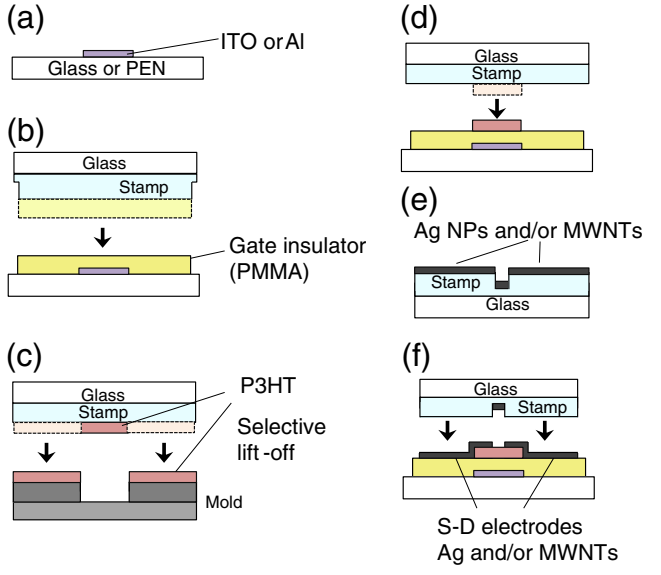

Fig. 1. Typical patterning and fabrication processes of P3HT-based FETs by soft lithography: (a) deposition and patterning of the gate electrode, (b) transfer printing of PMMA, (c) selective lift-off process of the P3HT film on the flat PDMS stamp, (d) transfer printing of P3HT, (e) deposition of Ag NPs and/or MWNTs on patterned PDMS, and (f) transfer printing of S–D electrodes.

3. Results and discussion

Fig. 2 shows the relationship between the drain current and source-gate voltage (transfer curves) for the ITO/PMMA/MWNT/P3HT (bottom contact) devices in which the P3HT layers were patterned and transferred at 65 and 100 °C, respectively. We presented both forward and reverse sweeps in order to visualize the existence of the hysteresis effect in the transfer properties. Moderate hysteresis behavior is observed for positive gate voltages. Table 1 summarizes the FET parameters obtained from Fig. 2, and the on/off ratio was calculated from the current ratio measured at a gate voltage of −40 and +20 V. Pattern transfer for the P3HT film was not reproducibly obtained at temperatures below 60 °C. At temperatures above 65 °C, P3HT was transferred onto PMMA-coated substrate with a pattern resolution of ca. 1 μm.

The transfer curves exhibit p-type semiconducting behavior, but an indispensable hole current is observed at positive gate voltages, especially in the device fabricated at 100 °C. Meijer et al. already reported that the conductivity of undoped P3HT is very low, and the hole current is observed only under accumulation mode at a negative gate voltage. On the other hand, the bulk conductivity of P3HT significantly increases when exposed to air due to the charge-transfer reaction with ambient molecular oxygen and is called p-type doping. At a positive gate voltage, holes in the bulk P3HT are depleted from the semiconductor layer, and no mobile charges are left to carry the current at the onset voltage V_{on} [28,29]. In the high-temperature process (transfer-printed P3HT at

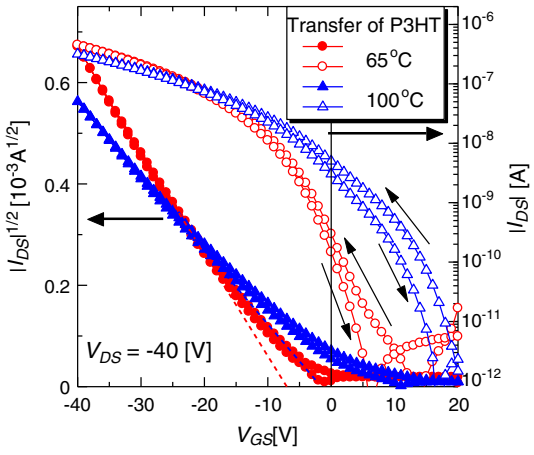

Fig. 2. Comparison of transfer curves for ITO/PMMA/MWNTs (S–D electrodes)/P3HT bottom contact FETs patterned the P3HT layer at 65 °C and 100 °C.