Solution processable micron- to nanoscale conducting polymer patterning utilizing selective surface energy engineering

Kwang-Ho Lee, Byung-Yeon Choi, Jeong-Woo Park, Seok-Ju Kang, Sang-Mook Kim, Dong-Yu Kim, Gun-Young Jung

A R T I C L E   I N F O

Article history:
Received 17 December 2009
Received in revised form 12 January 2010
Accepted 15 January 2010
Available online 21 January 2010

Keywords:
Conducting polymer
Surface energy
Organic field-effect transistors
Nanoscale patterning

A B S T R A C T

We developed a new conducting polymer microscale and nanoscale patterning method; a bottom-up approach for applying a conducting polymer solution on a substrate with locally varied surface energies. Selective surface energy engineering was achieved by combining conventional photolithography and local hydrophobic treatments with a self-assembled monolayer (SAM) at the exposed surface. The regions under the photoresist patterns remained hydrophilic after the photoresist removal. Here, a poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) conducting polymer solution was dispensed with a razor blade on the substrate, wetting only the hydrophilic regions. Next, conducting source/drain polymer electrodes were fabricated (channel length: 5 μm) and utilized for poly(3-hexylthiophene) (P3HT) organic field-effect transistors. For nanoscale conducting polymer line patterns, a photoresist template with nanoscale features was fabricated using holographic lithography. Finally, multi-step spin coating method reliably produced polymer lines having a linewidth of 292 nm at 1 μm spacing.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Conducting polymers have the potential to be widely used as electrodes in the fabrication of organic devices such as sensors, actuators, capacitors, and display devices [1,2]. As a result, these polymers have received considerable interest due to their intrinsic flexibility, thereby enabling the construction of flexible devices, as well as their ease of mass production, low cost, light weight, and solution processing at low temperature. For this reason, there have been attempts to develop unconventional patterning techniques for active or passive organic devices in the new era of plastic electronics [3].

However, conducting polymer patterning is the bottleneck in the path to the development of these wider applications. Conventional photolithography techniques require conducting polymers that are photosensitive and cross-linkable during UV exposure, if they are to remain intact during the subsequent development process; these restrictions demand the development of new material designs compatible with the process [4]. Jung et al. demonstrated conducting nanolines by combining the conventional lift-off process with a nanoimprinted poly(methyl methacrylate) template, where a charged conducting polymer anchored to an oppositely charged self-assembled monolayer (SAM) formed only at the trenches of the polymer template [5]. This process is not versatile, however, because the lift-off solvent could also dissolve the polymer film and/or degrade its conductance.

Alternatively, direct patterning techniques such as μ-contact printing [6], ink-jet printed patterning [7], dip-pen lithography [8], and gravure printing [9] have been introduced. In attempt to resolve this issue, Rogers et al. [10] and Someya et al. [11] demonstrated submicrometer patterns by injecting subfemtoliter ink through a nozzle...
sophisticatedly manufactured from a very fine capillary glass tube having a tip diameter of <1 μm.

In contrast to top-down process, Tessler et al. reported a bottom-up approach for conducting polymer patterning based on a hydrophobic SAM formed on a 80 nm thick TiO₂-covered substrate [12]. The SAM exposed to UV light through the photomask became hydrophilic due to the photocatalytic effect of TiO₂ in the exposed regions and enabled the solution-deposition of the conducting polymer via dewetting from the hydrophobic regions during subsequent spin-casting. However, this technique requires a thin TiO₂ layer for the photocatalytic reaction with SAM at a humidity of ca. 40%. Other dewetting techniques had hydrophobic regions defined by microcontact printing for ~3 μm patterning [13] and electron-beam lithography for a 500 nm transistor channel length [14]. However, it should be noted that electron-beam lithography is costly and time-consuming process for large-area applications.

In this work, we propose a hybrid process that combines conventional photolithography and local surface energy modification through hydrophobic treatment in order to fabricate nanoscale conducting polymer patterns by holographic lithography and the subsequent development process. (b) OTS attachment to the exposed substrate surface by self-assembly. (c) After removal of the PR patterns. (d) Conducting polymer solution dispersion; only hydrophilic regions are wet.

**2. Experimental section**

**2.1. Selective surface energy treatment for microscale polymer patterning**

The proposed fabrication process is shown in Fig. 1. In brief, a 50 nm thick silicon oxide (SiO₂) surface on a heavily doped n-type silicon substrate was successively cleaned with acetone, ethyl alcohol, and deionized water in an ultrasonic bath. For the initial hydrophilic surface modification, an oxygen plasma treatment was carried out at 300 W for 60 s. A positive tone PR (AZ6612, Clariant) solution was spin-coated on the substrate at 2800 rpm for 30 s and then baked at 100 °C for 1 min. A UV light (λ = 365 nm) irradiated the PR film for 6.7 s through a clear-field photomask on which the desired patterns had been chromium-deposited. After development process, a gentle oxygen plasma treatment was performed at 100 W for 30 s in order to remove any residual PR layer under the trenches and generate hydroxyl groups at the exposed surfaces, which anchor the hydrophobic molecules during the SAM treatment.

The substrate with the PR patterns was immersed into an octadecyltrichlorosilane solution (OTS; 1.5 wt.% in toluene) for 5 min. At above 1.5 wt.%, aggregated OTS molecules were observed in all of the exposed regions. At less than 1.5 wt.%, the wettability contrast did not provide sufficient definition, especially for the 5 μm channel length, resulting in current leakage between the source and drain electrodes. During the OTS SAM coating, the head groups (–SiCl₃) reacted with the hydroxyl groups on the substrate surface in the trenches via siloxane linkage, and the alkyl chains underwent van der Waals interaction between each other with the hydrocarbon tail groups (~CH₄) exposed to the air, thereby rendering the surface hydrophobic nature. The substrate was then baked at 120 °C for 10 min to remove any residual toluene solvent. After PR pattern removal by acetone soaking for 5 min in an ultrasonic bath, the protected regions underneath the PR patterns remained hydrophilic during the photolithography process and the subsequent OTS treatment. Thus, a substrate with locally varied surface energies was achieved and subsequently utilized for spontaneous polymer patterning.

As a conducting polymer solution, we adopted the aqueous poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) polymer solution (1:2.5 by weight, 1 wt.% solid content, BAYTRON®, PH 500) due to its excellent processing ability, as well as its conducting, transparent, and thin film characteristics. Recent studies have shown that the conductivity of PEDOT:PSS can be dramatically increased with no loss in optical transparency through the addition of a small amount of diethylene glycol dopant [15,16]. In this experiment, diethylene glycol was mixed with PEDOT:PSS (1:10 by volume), and the solution was then dropped and dragged on the specially treated substrate using the doctor-blade method with a razor edge; there were no notable effects of blading direction relative to the feature geometries. The solution was dewetted by the hydrophobic regions and was thus spontaneously confined in the hydrophilic regions during spreading. Next, the sample was left in air for 2 min to allow the solvent to evaporate; at this time the polymer solution contracted, reducing the surface energy, which resulted in contours with sharp edges at the corners. Finally, the conducting polymer patterns were heated at 110 °C for 10 min to increase the conductivity for subsequent use as the source and drain electrodes of OFETs.

**2.2. Nanoscale polymer patterning**

Laser interference lithography (i.e., holographic lithography) was used to fabricate nanoscale periodic PR patterns because it can produce nanoscale features with ease. In brief, a diluted positive PR (AZ6612, Clariant) with...
a thinner (AZ1500, Clariant) (volume ratio = 1:2) was spin-coated to a 150-nm thickness on a clean substrate that had previously been coated with hexamethyldisilazane (HMDS; above 98%, Fluka). Next, one-beam interference lithography method was utilized at an incident angle ($\theta$) of 7.18 to fabricate repeated PR line patterns having a line-width of 290 nm at a 1.3 μm pitch size. A UV laser beam from the He–Cd ion laser (325 nm) was then passed through a spatial filter consisting of several lenses and a pin hole (10 μm diameter) in the end, where diffraction-limited beam enhancement occurs; this enhanced beam was projected onto the angle bracket where the sample holder and Lloyd mirror were placed perpendicular to each other. The PR was exposed to light for 50 s, equivalent to a dose of 30 mJ/cm$^2$, with a sinusoidal intensity owing to the constructive and destructive interference between the two split beams, one directly from the laser and the other reflected from the Lloyd mirror.

A specific pitch size was determined by $A = \lambda / 2 \sin \theta$, where $\lambda$ is the wavelength and $\theta$ is the angle of incident laser. $A$ is the pitch size of the pattern, $\lambda$ is the laser wavelength, and the exposure time was optimized for the specific line width. After laser exposure, a developing process was performed by dipping the entire substrate into MIF 300 solution for 30 s and then rinsing with deionized water.

Next, the valve supplying the vapor of the hydrophobic material was closed and a second needle valve connected to a container partially filled with DI water was opened immediately after PR pattern removal. This selective surface engineering drives the spontaneous patterning of the conducting polymer solution, covering energetically unstable surfaces of hydrophilic regions with a high surface energy.

### 3. Results and discussion

#### 3.1. Surface energy measurement

To investigate the surface energy variation at each process step, the contact angle was measured with water at room temperature and then converted into surface energy using the Good–Girifalco–Fowkes–Young (G–G–F–Y) equation [20]:

\[
(1 + \cos \theta) \gamma_{LV} = 2(\gamma_{SV} V_{LV})^{1/2}
\]

where $\gamma_{LV}$ is the surface tension of the test liquor (water: 72.8 dyne/cm), $\theta$ is the contact angle, and $\gamma_{SV}$ is the surface energy of the medium of interest. Table 1 presents the results of contact angle measurements and their corresponding calculated surface energies at each step.

The initial surface treatment with oxygen plasma gas produced a very hydrophilic surface with a contact angle of 2.2°, equivalent to a high surface energy of 89.8 mN/m. The contact angle of the exposed substrate surface after development increased to a value of 14.2°. The surface became hydrophobic after application of the OTS SAM coating, attaining a contact angle of 97.7°, equivalent to a surface energy of 16.8 mN/m; this region was thermodynamically stable such that the surface is unlikely to react to other chemical elements.

The initial hydrophilic nature of the region under the PR pattern remained after PR removal, though the value increased to 26.8° due to the instability of the surface Si–OH groups with time. During the sequential processes for PR patterning and removal, the increase in contact angle is associated with a decrease in hydroxyl group coverage on the surface through the dehydration reaction between two neighboring hydroxyl groups, leading to the formation of a siloxane (Si–O–Si) bond [21]. The contact angle was 15° immediately after PR removal, and increased to 26.8° after 10 min in air. As such, polymer solution dispersion was completed within 10 min after PR removal. This selective surface engineering drives the spontaneous patterning of the conducting polymer solution, covering energetically unstable surfaces of hydrophilic regions with a high surface energy.

<table>
<thead>
<tr>
<th>Experimental process</th>
<th>Contact angle (°)</th>
<th>Surface energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial oxygen plasma treatment</td>
<td>2.2</td>
<td>89.8</td>
</tr>
<tr>
<td>Exposed area</td>
<td>After development</td>
<td>14.2</td>
</tr>
<tr>
<td>Exposed area</td>
<td>After OTS treatment</td>
<td>97.7</td>
</tr>
<tr>
<td>Protected area</td>
<td>After PR pattern removal</td>
<td>26.8</td>
</tr>
<tr>
<td>On PEDOT:PSS film</td>
<td></td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table 1: Contact angle measurement and corresponding surface energy calculated at each step.
The contact angle of the DEG-PEDOT:PSS film deposited on the hydrophilic region was also measured using water. Water was dropped through a syringe and wet the DEG-PEDOT:PSS film at a contact angle of 7.6°, corresponding to a surface energy of 89 mN/m. This illustrates that the DEG-PEDOT:PSS solution has a high affinity to water, which is driving force for spontaneous wetting in the localized hydrophilic regions.

3.2. Results of microscale polymer patterning

Fig. 2a presents SEM images of conducting polymer patterns (500 \( \mu \)m × 1000 \( \mu \)m) at gaps ranging from 5 to 100 \( \mu \)m. The polymer patterns exactly reproduce the corresponding photomask patterns via the proposed patterning method. The solution wets the pre-determined hydrophilic areas. The significant outcomes are that the gap is clearly defined along the 1000 \( \mu \)m length even at 5 \( \mu \)m gap and that no cracks are observed within the polymer patterns.

Fig. 2b shows the AFM image of the surface morphology of the 20 \( \mu \)m gap, where it can be seen that the conducting polymer solution is well confined at the hydrophilic region at that resolution during dispersion. Fig. 2c represents the thickness profile of the polymer pattern measured by surface profiler (Alpha-Step IQ, KLA Tencor); the polymer electrode has a maximum thickness of 380 nm at the center. When a liquid interfaces with air, the molecules at the interface have a higher energy than that of the interior molecules; therefore, the eventual curvature of the thickness profile shown in the figure is formed to minimize the surface area and thereby reduce its surface energy.

These conducting polymer patterns were subsequently used as the source/drain electrodes in OFET devices. Using the four-point probe method, the conductivity of the conducting polymer pattern was measured to be ca. 400 \( \times \) 10\(^2\) S/cm. The polymer electrodes for the bottom contact OFETs (BC-OFET) were fabricated on top of a 50-nm thick gate insulating layer of silicon oxide that was grown on the heavily doped n-type silicon substrate. A prior study investigating the surface-treatment effects on the performance of OFETs indicated that OTS treatment of the gate dielectric layer increased the crystallinity of the semiconducting active material and hence carrier mobility [22]. In our case, as the exposed silicon oxide surface between the source/drain polymer electrodes was already coated with OTS during the selective hydrophobic treatment, 1 wt.% of P3HT solution in chloroform was spin-coated without further treatment and then baked at 125 °C for 20 min inside a nitrogen glove box.
The charge carrier mobility in the saturation region is determined by the equation:

\[ \mu = \frac{W}{L} \frac{I_D}{V_{GS}-V_T} \]

where \( C_i \) is the capacitance per unit area of gate insulator (50-nm thick silicon oxide, 69 nF/cm²), \( W/L \) is the ratio of channel width to channel length, \( V_T \) is the threshold voltage, \( I_D \) is the drain current, and \( \mu \) is the charge carrier mobility of the OFET. For our device, the charge carrier mobility was calculated to be \( 1.4 \times 10^{-3} \text{ cm}^2/\text{V s} \) at a threshold voltage of 0.2 V and an on/off current ratio of \( 1.2 \times 10^4 \). With increasing the channel length, the mobility was enhanced to \( 2.5 \times 10^{-2} \text{ cm}^2/\text{V s} \) at a threshold voltage of 0.2 V and an on/off current ratio of \( 1.2 \times 10^4 \). With increasing the channel length, the mobility was enhanced to \( 2.5 \times 10^{-2} \text{ cm}^2/\text{V s} \) at a threshold voltage of 0.2 V and an on/off current ratio of \( 1.2 \times 10^4 \). With increasing the channel length, the mobility was enhanced to 3 cm²/V s at a threshold voltage of 0.2 V and an on/off current ratio of \( 10^3 \).

3.3. Nanoscale polymer line patterning

Fig. 4a shows the SEM image of separate PR line patterns after development with a linewidth of 290 nm, spacing of 1 µm, and a thickness of 120 nm, which was fabricated using an interference lithography technique. Its corresponding AFM image (Fig. 4b) illustrates a PR template ready for the local surface energy treatment.

After hydrophobic treatment in vapor phase, several trials using the doctor-blade method for polymer solution dispersion ended up with no polymer patterning at such a tiny scale; the solution covered the whole substrate because the generated solution film was too thick to be confined into the nanoscale hydrophilic line areas. Instead, a multi-step spin-coating method was utilized to produce nanoscale polymer patterns. Preliminary experiments with single-step casting at a low spin speed generated polymer coverage over the entire substrate similar to the doctor-blading results; at a high speed, all the polymer solution was spinned off before the substrate surface was wetted. Therefore, the spin speed was stepwise increased in order to provide a relaxation period to allow the polymer solution to equilibrate to the local surface energy.

Fig. 4c shows that the polymer line patterns are well matched with the feature size of the PR template; 292 nm wide lines at 1 µm spacing. However, some polymer residue can still be seen between the polymer lines in the AFM image (Fig. 4d). The cross-sectional surface profile (Fig. 4e) illustrates that 30 nm thick polymer nanolines were generated by using the multi-step spin-coating method.

4. Conclusions

In summary, a new process for conductive polymer patterning that combines conventional photolithography and self-assembly monolayer deposition of a hydrophobic material was proposed. As the regions protected by the
photoresist patterns remained hydrophilic following the photoresist removal, a chemically patterned substrate with locally different surface energies was generated. Based on this process, we fabricated P3HT organic semiconducting field-effect transistors using the PEDOT:PSS source/drain electrodes formed by selective dewetting. The device showed a comparable transistor performance to previous devices: a field-effect mobility of $1.4 \times 10^{-3}$ cm$^2$/V·s; a threshold voltage of 0.2 V; and on/off current ratio of $10^4$ at a 5 µm channel length. In addition, the polymer solution effectively wetted the nanoscale hydrophilic regions, predetermined by holographic lithography and subsequent selective hydrophobic treatment in vapor phase. As a result, nanoscale polymer lines with a linewidth of 292 nm at 1 µm spacing were reliably fabricated by the multi-step spin-coating method. In the near future, it is expected that this technique could be applied to solution-processible plastic electronics.

**Acknowledgements**

This work was partially supported by the Ministry of Knowledge Economy (MKE), Korea through a project of the Research Consortium for R2R printed RFID tags and the System IC 2010 project from the Ministry of Commerce, Industry and Energy (MCIE), Korea. This work was also supported by the Korea Science and Engineering Foundation (KOSEF) grant (No. R15-2008-006-03002-0, CELA NCRC), and the Program for Integrated Molecular System at GIST.

![Fig. 4. (a) FE-SEM image of the nanoscale PR features produced by holographic lithography and (b) its corresponding AFM image. (c) FE-SEM and (d) AFM images of the nanoscale polymer line patterns with a width of 292 nm at 1 µm spacing produced by using the polymer template of (a). (e) Cross-sectional surface profile of the polymer line patterns.](image-url)
References