Fabrication of Vertical Organic Junction Transistor by Direct Printing Method

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An organic junction transistor with a vertical structure based on an active layer of poly(3-hexylthiophene) was fabricated by facile micro-contact printing combined with the Langmuir-Schaefer technique, without conventional e-beam or photo-lithography. Direct printing and subsequent annealing of Au-nanoparticles provided control over the thickness of the Au electrode and hence control of the electrical contact between the Au electrode and the active layer, ohmic or Schottky. The junction showed similar current-voltage characteristics to an NPN-type transistor. Current through the emitter was simply controllable by the base voltage and a high transconductance of ~0.2 mS was obtained. This novel fabrication method can be applied to amplifying or fast switching organic devices.

Key Words: Organic junction transistor, Poly(3-hexylthiophene), Micro-contact printing, Au-nanoparticle, Langmuir-Schaefer technique

Introduction

Organic semiconductors are being developed as they have interesting potential applications in such as flexible devices. Conjugated polymers and molecules have been used in the fabrication of organic transistors, with pentacene a common choice due to its having the greatest known mobility (~2 cm²/Vs) of an organic material for high-current driving circuits.¹

Pentacene has only been deposited by thermal evaporation in vacuum but organic semiconductors which can be processed in solution phase at room temperature under atmospheric pressure are more attractive and can offer varied potential applicability in flexible devices. Despite having a hole mobility of ~0.1 cm²/Vs, much lower than that of pentacene, a regio-regular substituted semiconducting polymer, poly(3-alkylthiophene), has shown solution processability due to its excellent solubility.²,³ Spin-coating, drop casting and the Langmuir-Blodgett (LB) method have been used to deposit polymer films. The LB method has been proposed for the deposition of molecular monolayer-scale films on various substrates, showing excellent thickness control and the formation of close-packed ordered films.⁴

Conventional lithography techniques such as e-beam or photo-lithography are widely used for the fabrication of integrated circuits and transistor arrays, though the required vacuum equipment makes them expensive. Recently, much simpler and cheaper patterning techniques based on printing methods such as ink-jet printing² and micro-contact printing (MCP)⁹ have been developed. MCP has been widely used for micro-scale patterning via the inking and printing of poly-dimethylsiloxane (PDMS) stamps. The strong interactions between the molecular ink and the functional groups of the substrate's self-assembled monolayer allow micro-patterns to be easily transferred to the substrates. Various self-assembling molecules,⁵ nanowires⁶ and nanoparticles⁷ have been used as inking materials, with gold considered an appealing electrode material given its operational stability and ability to form excellent ohmic contacts with most p-type organic semiconductors used in organic thin film transistors.⁸ Loo and Rogers reported the direct transfer of Au films via MCP with evaporated Au on a patterned stamp.¹¹ A self-assembling close-packed monolayer of Au-NPs can be formed over a large area of a water surface.¹² Such an Au-NP monolayer could be transferred by the Langmuir–Schaefer (LS) technique, which entails bringing a substrate parallel to the water surface and allowing it to touch the film lightly.

This work reports the fabrication of a vertical organic junction transistor (OJT), with an active layer of poly(3-hexylthiophene) (P3HT), via the direct patterning of Au-NP electrodes without any other lithographic techniques. The transistor was expected to have higher current flow through its channel compared with ordinary high-speed planer type transistors, owing to its shorter channel length and larger effective channel area.¹³ The three electrodes of the device, base, emitter, and collector, were formed by transferring Au-NP patterns via the MCP of Au-NP layers in a LB trough. Controlling the thickness of the Au-NP electrodes allowed control of the electrical contact, ohmic or Schottky, between the electrode and the active P3HT layer. The resulting OJT showed the I-V characteristics of an NPN-type transistor with a high transconductance of ~0.2 mS.¹⁴,¹⁵

†This paper is to commemorate Professor Myung Soo Kim's honourable retirement.
Experimental

Synthesis of Au-NPs and LB Film. Octanethiol capped Au-NPs were synthesized by Burst method. Their average diameter was estimated to be 6.2 ± 2.5 nm from TEM images obtained with an electron energy of 200 keV (Philips Tecnai F20). Flexible polycarbonate substrates were from LG electronics Co. A KSV 2000 Langmuir trough was used for formation of Au-NP films. AFM images were obtained with an XE-100 (PSIA). X-ray photoelectron spectroscopy (XPS) was with an ESCALAB 150 instrument (ThermoVG, UK).

Fabrication of Au-NP Electrode. The LB trough was filled with DI water and 500 mL Au-NP solution (0.5 mg/mL) was spread over the water surface. After the evaporation of chloroform for at least 1 h, Au-NPs on the surface were compressed by a barrier at a rate of 10 mm/min. At a surface pressure of 15 mN/m, the patterned PDMS stamp horizontally made contact with the Au/water surface. The PDMS stamp, inked with Au-NPs, was then carefully pressed onto the substrate to transfer the Au-NP patterns. After the Au-NP patterns were deposited, they were annealed in a vacuum oven at 170 °C for 2 h. P3HT film was then transferred onto the Au/Si substrate by MCP. The base electrode, with an open square pattern, was subsequently fabricated by MCP using a PDMS stamp with a mesh pattern (Figure 1(b)). The transferred mesh-type base Au-electrode was visible by AFM (Figure 1(c)). The base electrode was designed to be 40-60 nm. The dark squares of the AFM image represent the exposed P3HT film not covered by the Au electrode. After annealing the substrate, a 2nd P3HT layer of ~200 nm was deposited by solution dropping using a micropipette (Figure 1(d)). A stripe patterned 70-100 nm thick collector electrode oriented perpendicular to the emitter was transferred onto the substrate by rotating the stamp by 90° (Figure 1(e)). The electrical contact between the Au-NP electrode and the p-type semiconducting P3HT film depended on the thickness of the electrode after thermal annealing under vacuum: below 60 nm Schottky contact formed; above 60 nm, ohmic contact formed. Therefore, the base electrode would be expected to form Schottky contacts both with the 1st P3HT layer.
layer and with the 2nd electrode. The contacts between the emitter and the P3HT, and that between the collector and the P3HT would be expected to be ohmic.

AFM images and line profiles of the patterned arrays of Au-NPs on SiO$_2$ and flexible polycarbonate (PC) substrates were recorded (Figure 2). PDMS stamps of various sizes were used to transfer the Au-NP patterns. The index “$a/b$” labeling the AFM images represents the stripes’ separation ($a$) and width (b), both in μm. The initial striped pattern had an index of 4/6 (Figure 2(a)). A crossed pattern was then produced by printing another striped stamp coated with Au-NPs on top of this pattern (Figure 2(b)). The line profile shows that the height of the overlap regions was twice that of the initial stripes. Similar repeated printing produced multilayers of various nanoparticles or nanomaterials with precise control over the properties of each layer. Au stripes in a uniformly arrayed nano-scale pattern were transferred with a 100 nm half-pitch, with the height of the Au pattern (~3 nm) which was measured to be lower than the size of Au-NPs (~6 nm), likely due to the tip size effect of AFM (Figure 2(c)). AFM image showed the striped Au-NP patterns on a flexible polycarbonate (PC) substrate to be 500 nm wide (Figure 2(d)). The surface of the bare PC substrate was quite rough at an atomic scale with a roughness of 3.2 nm as shown in the inset. These results show that the sub-micron scale patterns of Au-NPs were also successfully transferred to the non-flat flexible PC substrate by using the elastomeric properties of the PDMS stamp.

Transmission electron microscopy (TEM) images of the three LS layers of Au-NPs were recorded without any treatment (top), after UV-irradiation for 30 min (middle), and after thermal annealing at 170°C in vacuum for 2 h (bottom), respectively (Figure 3(a)). Both UV exposure and thermal annealing in vacuum induced aggregation of the Au-NPs, with much greater aggregation observed after annealing than after UV treatment. The thickness of the Au-NP pattern was controlled layer-by-layer (Figure 3(b)), with thickness increasing linearly with the number of stampings of the LS layer of Au-NPs on the water surface. The thickness of the transferred Au-NP pattern was reduced by thermal annealing due to the coagulation of Au-NPs because of the removal of capping thiol molecules. Thermal annealing under vacuum effectively induced aggregation, allowing precise thickness control through the number of stampings. UV-irradiation, however, was effective only up to ~5 LS layers of Au NPs since it could not penetrate deeply into the thicker film.

![Figure 3](image-url)
XPS spectra of ten LS layers of Au-NPs (Figure 3(c)) show peaks at 160–165 eV, corresponding to gold–sulfur binding. After UV-irradiation, much of the Au-S peak decreased but the peak at ~168 eV, corresponding to sulfonate (S-Oₓ) increased. Rinsing the UV-irradiated Au slightly diminished the sulfonate peak. The vacuum-annealed sample showed no sulfonate peak and a much smaller thiol peak. The ratio of atomic concentrations of the vacuum annealed and as deposited samples, S_{vacuum annealed} / S_{as deposited}, was 1/4, attributable to the thermal desorption of the capping thiol molecules in the vacuum oven.

TEM images (Figure 3(a)) and XPS spectra (Figure 3(c)) showed that thermal annealing under vacuum induced coagulation of the Au-NPs and effectively removed the thiol molecules capping them, which greatly reduced the sample's electrical resistance (Figure 3(d)). The electrical resistance measured across the Au-NP line patterns after vacuum annealing at 170 °C significantly decreased with increasing thickness. Considering that the resistance of a homogeneous film is given by $R = \frac{1}{\sigma \times \omega \times l}$, where $\sigma$ is its conductivity, $\omega$ its length, $l$ its width, and $t$ its thickness, the cross product of resistance and thickness should be constant irrespective of thickness ($Rt = \frac{1}{\omega \times l}$). However, the discrepancy of the products of the measured resistances and the thicknesses with that of bulk gold as shown in Figure 3(d) indicates that the conductivity was reduced in the thinner Au-NP electrodes. As the thickness of the film increased, the grain size increased to reduce the inter-grain path for conduction as shown in Figure 3(e). In addition, larger holes were observed as the thickness increased, which could affect the electrical conductivity of the film since the effective area of the electrode might have been reduced. However, we cannot quantitatively compare its influence on the electrical conductivity for the films with different thickness since we do not estimate the total area of the holes. Therefore, the thickness dependent $Rt$ value shown in Figure 3(d) is attributed to the increased inter-grain paths for conduction in the thinner electrodes, consistent with their smaller grains (Figure 3(e)).

SEM images of the annealed Au-NP electrodes of various thicknesses show that their grain sizes increased as thickness increased from 40 nm to 60 nm (Figure 3(e)), though there was no great change in grain size as the films further increased in thickness to 80 nm. The changes in grain size correspond to the observed changes of conductivity with thickness. A resistance below 10 $\Omega$ could be obtained with the 60 nm thick vacuum annealed Au-NP patterns. Four point probe measurements ascertained the electrical conductivity of the 60 nm thick vacuum annealed sample to be $1.5 \times 10^5$ S/cm, close to that of conventionally evaporated 70 nm thick pure Au,$^{19}$ $2 \times 10^5$ S/cm and bulk Au at room temperature. This implies that vacuum annealed Au-NP patterns thicker than 60 nm could be used practically as electrodes in electronic devices.

The applicability of the Au-NP patterns as electrodes was tested in the fabrication of a vertical OJT. The influence of the separation of the gold islands on electrical resistance could aid the engineering of the device's electrical and contact properties. Given that the thiol molecules capping the Au-NPs could act as energy barriers that would reduce the penetration of the wavefunction, the electrical contact with the semiconductors may change due to the different concentrations of sneak charges at the insulating and semiconductor sides. Bardeen’s model$^{10}$ suggests that the existence of insulating barriers can significantly influence Schottky barriers, giving soft reverse characteristics. Therefore the varying separations of the Au-NPs due to the different amounts of remaining thiol molecules after annealing could change the shape of the potential barriers and the electrical contacts.

Nano-devices’ stable and reproducible operation requires the fabrication of suitable electrical contact between the electrodes and the active layer, containing such as nanowires and organic thin films. Assuming the variation of contact barrier properties described above, the dependence of the electrical contact properties of the Au-NP electrodes on thickness was investigated in a vertical structure consisting of top- and bottom-Au electrodes either side of a P3HT active layer (Figure 4(a)). The thickness dependence of current-voltage (I-V) characteristics was assessed by testing several sets of vertical structures with various thicknesses of Au-NP electrode. An Au electrode of ~40 nm thickness resulted in Schottky contact between the Au and P3HT, with soft-reverse characteristics; contact was ohmic when the thickness was ≥ 60 nm (Figure 4(b)). Examination of only the work-functions of bulk Au and p-type P3HT does not explain why the thin Au-NP layers make Schottky contact with P3HT. Ruffino et al. reported that the height of the Schottky barrier between Au-NPs and SiC depended on the

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**Figure 4.** (a) The vertical structure comprising top and bottom Au-NP electrodes with P3HT active layer between and its contact properties with varying electrode thickness. (b) Current-voltage characteristics for the ohmic (filled circles) and Schottky (open circles) contacts marked in the Table. (c) The dependence of contact barrier on the thickness of the granular Au-electrode. $\Delta \Phi$ denotes the contact barriers and $T$ the tunneling probability which contribute to the conduction of current. (d) The temperature dependence of the resistance between the top and bottom electrodes.
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particles' sizes: smaller Au-NPs showed decreased work functions, affecting the Schottky barrier with the p-type semiconductor. Figure 4(c) outlines how thickness could have affected contact properties in terms of the varying work-function (ΔΦ) in the granular Au-NP electrodes. Decreasing the size (D) of the Au-NPs can raise the Fermi level (E_F) due to quantum confinement and charging, increasing the effective Schottky barrier (ΔΦ) by the alignment of the Fermi levels. Therefore larger grains of Au-NPs could have shown smaller barrier heights that would have led to the ohmic behavior. As the average thickness of the insulating layer (t) decreased, the depletion layer (λ) decreased, increasing the probability of tunneling (T), which could account for the reduction of resistance after the thermal or UV treatments. The balancing of thermionic conduction and tunneling conduction could dominate the electrical properties.

To confirm that the ohmic shape of the I-V characteristics of the thick Au-NP electrodes was not due to an electrical short between the top and bottom electrodes, the temperature dependence of the resistance of several samples was measured. The consistent semiconducting behaviors (Figure 4(d)) demonstrate that the ohmic contact was not through metallic shorting. Therefore the ohmic behavior of the thicker Au samples was attributed to the ohmic contact and not a short circuit.

Rectifying I-V curves of the junction show an apparent turn-on voltage of around 0.5 V (Figure 5(a) and (b)). The forward bias is defined as the higher potential at the organic channel assuming Schottky barriers at the top or the bottom electrodes. The significant reverse current, i.e., soft reverse characteristics, was due to various barrier lowering mechanisms such as surface states or insulating barriers at the contacts. From the polarity of the forward bias, the equivalent circuit of the OJT could be modeled as an NPN-type transistor (Figure 5(c)). Considering the junctions in the transistor structure, the three terminals can be labeled as emitter (E), collector (C) and base (B) for the buried electrode. The current-voltage (I-V_CE) characteristics of the vertical OJT were measured with varying base voltages (Figure 5(d)). I_E and V_CE are defined as current from the emitter and the potential difference applied between the collector and the emitter, respectively. The finite current at zero V_CE comes from the injection of current by the base-emitter bias, V_BE.

The transistor's operation mode can be analyzed in the saturation regime owing to the forward biases of the pairs B-E and B-C, which can be used for switching. The saturation plateau of I_E-V_CE could be maintained by the current flow from the base to the collector, contributing no change of current at the emitter. Further decreasing collector voltage lowers the voltage of the base electrode, reducing the emitter current at the negative V_CE owing to the decrease of V_BE. Therefore the resultant saturation behavior with the V_CE bias voltage can be applied to switching circuits in depletion mode. The OJT fabricated here is expected to be applicable in electronic devices such as amplifiers or switches that require high-currents or high-speeds for use in such as the active devices of display circuits.

Conclusion

A vertical type organic junction transistor was fabricated via direct patterning by MCP with the LS method. It exhibited high transconductance with a current of mA upon the application of a few volts. The junction's performance was consistent with that of an NPN-type transistor. The junction's high performance was possible through the control of the electrical contact properties between the Au-NP electrode and the semiconducting P3HT film by precise control of the thickness of the Au-NP electrode. This work represents the basis of a novel fabrication of amplifying devices by simple printing.

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