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# Effect of gate electrode conductivity on operation frequency of inkjet-printed complementary polymer ring oscillators

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ABSTRACT

We report the effect of the conductivity of the gate electrode on operation speeds in printed organic ring oscillators (RO). The highly conducting gate electrode leads to a superior oscillation frequency (as high as ~30 kHz) for the printed ROs. Above the optimum thickness of the gate electrodes (~30 nm), inkjet-printed p-type poly(3-hexylthiophene) (P3HT) and n-type poly([*N*,*N*-9-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,59-(2,29-bithiophene)) (P(NDI2OD-T2)) organic field-effect transistors showed reasonably high hole and electron mobilities of ~0.05 $cm^2 V^{-1} s^{-1}$ and ~0.25 $cm^2 V^{-1} s^{-1}$, respectively. Complementary inverters and ring oscillators based on these p- and n-type semiconductor transistors were constructed, where the inverters showed the inverting voltage, ($V_{inv}$) near the ideal switching points at 1/2 the drain voltage ($V_{DD}$), high gain (~10), low static power consumptions, as well as high noise margin (~60% of 1/2$V_{DD}$). Finally, printed P3HT complementary ring oscillators with a gate thickness over 30 nm exhibited the highest oscillation frequency (~30 kHz).

## 1. Introduction

In the past two decades, remarkable progress in organic electronics and optoelectronics has been achieved using π-conjugated organic semiconductors. The unique advantages of these organic materials, including mechanical flexibility, the fine tuning of their properties by versatile molecular design and chemical synthesis, as well as their straightforward solution processability, enable a variety of unconventional flexible and stretchable optoelectronic applications via simple and low-cost graphic-art printing processes [1]. In particular, solution-processed organic field-effect transistors (OFETs) are crucial components in a majority of promising printed electronic device applications, such as digital and analog circuits in radio frequency identification tags, drivers of flexible active-matrix displays, sensors, and non-volatile memory [2–5]. Importantly, the versatile applications of solution-processed OFETs are predominantly determined by the operation speed of the individual devices and integrated circuits. Although promising field-effect mobilities ($\mu_{FET}$) of over 3 $cm^2 V^{-1} s^{-1}$ (for polymers) and 10 $cm^2 V^{-1} s^{-1}$ (for single crystals) have been achieved in state-of-the-art OFETs [6,7], most low-mobility organic semiconductors still remain to be employed in suitable applications.

The electrical performance of OFETs is mainly determined by the intrinsic properties of the organic semiconductors as well as their thin film morphologies, and the interface properties between semiconductors and charge injection electrodes or semiconductors and gate dielectrics [8]. In addition, the circuit configuration (unipolar or complementary), device architecture (coplanar or staggered), the dimensions of the active channel (such as the channel's width/length ratio (*W*/*L*)), and the overlap between the gate and source/drain (S/D) electrodes ($L_{overlap}$), might also critically affect the overall performance of the electronic circuits [9]. The transition frequency ($f_T$) of the individual transistor is given by Eqs. (1)–(3):

$$f_T \approx \frac{g_m}{2\pi C_G} = \frac{\mu}{2\pi L\left(2L_{overlap}+\frac{2}{3}L\right)}(V_{GS}-V_{Th}) \qquad (1)$$

$$g_m \approx \mu C_{ox}\frac{W}{L}(V_{GS}-V_{Th}) \qquad (2)$$

$$C_G \cong 2C_{overlap}+\frac{2}{3}WLC_{ox} = 2WL_{overlap}C_{ox}+\frac{2}{3}WLC_{ox} \qquad (3)$$

where $C_{ox}$ and $V_{Th}$ are the gate dielectric capacitance and threshold voltage, respectively. Furthermore, for more complex electronic circuitry, including complementary inverters and ring oscillators, electrical conductivities of the gate, S/D electrodes, and the interconnects that bridge the transistors become important parameters. Obviously, the resistive–capacitive delay hinders any further increase in the speed of state-of-the-art microelectronic integrated circuits, and it will also present a serious problem when the complexity and down-scaling of the feature sizes of the printed organic electronic devices and integrated

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circuits are increased [2]. Most conductive inks typically used in flexible and printed electronics applications, such as conducting polymers, metal pastes, and transparent conducting oxides, have a higher resistance than conventional bulk metal electrodes do. The low conductivities found in the printed conductive materials constituting the electrodes and interconnects may cause certain problems for the development of high-performance organic electronic devices and circuits based on graphic-art printing processes [10]. Therefore, the effects of electrode conductivity on the physical characteristics of the printed electronic devices and circuits should be studied.

In this paper, we investigate the effects of the conductivity of the gate electrode and the interconnects on the operation speeds of printed organic ring oscillators. The sheet resistance of the gate electrodes was controlled by simply varying the thicknesses of thermally evaporated Au films. We found a strong correlation between the conductivity of the gate electrode and the operation speed of printed organic ring oscillators. Above the optimum thickness of the gate electrodes (~30 nm), the inkjet-printed p-type poly(3-hexylthiophene) (P3HT) and n-type poly([*N*,*N*-9-bis(2-octyldodecyl) naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,59-(2,29-bithiophene)) (P(NDI2OD-T2)) OFETs showed reasonably high hole and electron mobilities of ~0.05 $cm^2 V^{-1} s^{-1}$ and ~0.25 $cm^2 V^{-1} s^{-1}$, respectively. Complementary inverters and ring oscillators were composed based on these p- and n-type semiconductor transistors, where the inverters showed the inverting voltage ($V_{inv}$) near the ideal switching point at 1/2 the drain voltage ($V_{DD}$), high gain (~10), low static power consumption, and high noise margin (~60% of $1/2V_{DD}$). Finally, printed P3HT:N2200 complementary ring oscillators with a gate thickness of over 30 nm exhibited the highest oscillation frequency (~30 kHz).

## 2. Experimental details

### 2.1. Field-effect transistor fabrication

Corning Eagle 2000 glass substrates were cleaned sequentially in an ultrasonic bath with deionized water, acetone, and isopropanol (10 min for each cycle). The gold/nickel (Au/Ni) (12 nm/3 nm thick) patterns for the S/D electrodes (Ni being the adhesion layer) were fabricated using a conventional lift-off photolithography technique. The p-type and n-type polymer semiconductors prepared from regioregular poly(3-hexylthiophene) (rr-P3HT, Rieke Metals, Inc.) and poly([*N*,*N*-9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,59-(2,29-bithiophene)) (P(NDI2OD-T2), Polyera Corporation), respectively, were used as received. P3HT and P(NDI2OD-T2) were dissolved in anhydrous chlorobenzene (CB) to obtain solutions of ~5 mg/ml. After heating overnight at 80 °C on a hotplate, the solutions were filtered through a 0.2 μm polytetrafluoroethylene (PTFE) syringe filter before use. The semiconductor solutions were spin-coated or inkjet-printed onto Au/Ni patterned substrates in air, while maintaining the substrates at room temperature using a custom-built research inkjet printer (UJ100MF, Unijet). A piezoelectric-type drop-on-demand dispensing head (Microfab Technologies) with a 50 μm orifice diameter was used at an operating frequency of 500 Hz. Inkjet-printed P3HT and P(NDI2OD-T2) films were annealed at 150 °C for 30 min in a $N_2$-filled glove box to remove residual solvent and to induce an optimized microcrystalline morphology of the films. For the polymer gate dielectric layers, poly(methyl methacrylate) (PMMA, Aldrich, MW = 120 kD) was used without further purification. PMMA (80 mg $ml^{-1}$) was dissolved in *n*-butyl acetate and the solution was filtered through a 0.2 μm PTFE syringe filter before being spin-coated at 2000 rpm for 1 min. After dielectric layer coating, the samples were finally annealed at 80 °C for 1–2 h in the same glove box to remove the residual solvent. Top-gated OFET devices were completed by forming gate electrodes (Al, 50 nm) on the PMMA-coated active regions via thermal evaporation with a metal shadow mask.

### 2.2. Complementary inverter and ring oscillator fabrication

The described Au/Ni S/D electrodes on glass substrates were used for building complementary inverters and ring oscillators with varying *W*/*L* ratios. Each p-type P3HT (5 mg/ml in CB) and n-type P(NDI2OD-T2) (5 mg/ml in CB) was sequentially inkjet-printed onto Au/Ni patterned substrates in air. S/D electrode patterning, inkjet-printing, and thermal annealing were performed using the same procedure as used for the fabrication of OFETs. After spin-coating the PMMA gate dielectric, pure solvent (CB) was inkjet-printed onto the PMMA-coated devices to make via holes. Top-gated and inkjet-printed complementary polymer ring oscillators were completed by the formation of gate electrodes via thermal evaporation of Au with various film thicknesses (~1–50 nm) using a metal shadow mask.

### 2.3. Characterization

The electrical and static characteristics of OFETs and complementary inverters were measured using a semiconductor parameter analyzer (HP-4156A) in a $N_2$-filled glove box. The $\mu_{FET}$ and the $V_{Th}$ were calculated at the saturation region ($V_d = \pm 60$ V) using gradual channel approximations [11]. The dynamic characteristics of the ring oscillators were measured using a DC voltage power supplier with a built-in oscilloscope system. Scanning electron microscope (SEM) images of the thermally deposited Au electrodes with different film thicknesses were obtained using an S-4800 SEM (Hitachi Co. Ltd.) while the sheet resistance of the Au gate electrodes was obtained using a four-point probe measurement (AiT Co. Ltd., CMT-SR2000N).

## 3. Results and discussion

Fig. 1a shows the molecular structure of the P3HT and P(NDI2OD-T2) semiconductors as well as the configuration of the top-gate/bottom-contact (TG/BC) OFET employed in this study. The TG/BC staggered geometry typically enables high charge carrier mobilities for both holes and electrons by proper selection of the gate dielectrics and the fact that the orthogonal solvents are free from specific mobile charge trapping moieties such as hydroxyl groups on $SiO_2$ [12]. Moreover, the relatively low contact resistance provided by the large charge injection area, the ambient stability improved by the overlaid gate dielectrics and gate electrodes, and most importantly, the easy formation of the gate electrodes on top of the gate dielectric layer, make this geometry perfectly suited for studying the effect of the conductivity of the gate electrode on the characteristics of printed organic electronic circuits. OFET devices were fabricated either by inkjet-printing or spin-coating methods, where the latter served for the construction of the reference device. Fig. 1b and c show CCD camera images of the P(NDI2OD-T2) ink droplet formation with delay times varying from 0 to 100 μs and the corresponding inkjet-printed active features of the Au S/D electrode patterned on a glass substrate, respectively. Here, we used optimized conditions to generate droplets with diameters of 30 to 33 μm and volumes of 15–19 pl at a drop velocity of 3.0–3.6 m $s^{-1}$. The printed conjugated polymer films typically showed the strong coffee ring effect which leads to uneven surface morphology. We already reported the effect of the rough surface, which is mainly induced by ink-jetting processes, on the characteristics of P3HT OFETs [13]. The height difference from boundary to center parts in the ink-jet printed conjugated polymer feature was around 10–30 nm [13]. However, the over-coated PMMA dielectric layer in top gated FET geometry is relatively thick enough (~400 nm) to make flat surface (rms roughness < 0.1 nm) for thin gate electrode film. Therefore, we can exclude the rough surface effect of ink-jet printed active layers even for the very thin gate electrode ~10 nm.