Air-stable organic complementary-like circuits

Abstract

Air-stable ambipolar field-effect transistors based on a small bandgap semiconductor (nickel dithiolene) are demonstrated. The stability and reliability allows for the fabrication of discrete CMOS-like inverters. By using a flexible substrate technology, flexible integrated inverters were obtained. Combining series of integrated inverters resulted into a CMOS-like ring oscillator demonstrating the feasibility of ambipolar based circuits.*

6.1 Introduction

To date there are two demonstrated technologies for the fabrication of organic integrated circuits: the unipolar and the complementary technology. Unipolar architectures consist of $p$-channel organic field-effect transistors (OFETs), which are simple to fabricate since they require a single, high-work function metal (e.g., gold) and a single semiconductor material, which can be either evaporated or solution-processed.\textsuperscript{1–4} Despite this great advantage, unipolar circuits have poor performance, exhibiting a narrow noise margin, low yield, and high power consumption.\textsuperscript{2} In order to improve their performance, more sophisticated architectures are usually employed.\textsuperscript{5} Although beneficial, such an approach increases circuit complexity by nearly 100 %. Complementary architectures, adopted from silicon microelectronics, solve this bottleneck by providing major advantages in circuit performance, including wide noise margin, robustness, and low power dissipation.\textsuperscript{6,7} Unlike silicon technology, however, fabrication of discrete organic $n$– and $p$–channel transistors with lateral dimensions of a few micrometers, typically required for largescale integration, is still very challenging.

We have shown recently that a promising route towards robust, organic integrated circuits is the complementary-like approach based solely on ambipolar transistors.\textsuperscript{8,9} However, a critical issue for all ambipolar transistors reported to date is the injection of both electrons and holes into the semiconductor from the same electrode material. This is due to the mismatch in the energy levels of the electrode and the semiconductor for at least one of the carriers.\textsuperscript{8,9} A common method for suppressing such injection barriers is the use of dissimilar metal electrodes, that is, a high- and a low-work function metal.\textsuperscript{10} Unfortunately, this approach makes circuit fabrication complex and potentially expensive. An additional drawback of known ambipolar semiconductors, and hence ambipolar transistors based upon them, is their extremely poor environmental stability.\textsuperscript{10–14} Because of these problems, reports on complementary-like organic circuits are limited to the quasistatic characterization of simple circuits under stringent experimental conditions.\textsuperscript{8,9,13} Here, we demonstrate the dynamic operation of integrated complementary-like circuits based on solution-processed ambipolar transistors.
6.2 Nickel dithiolene transistors

As the organic semiconductor, we have employed the soluble, near-infrared-absorbing dye bis(4-dimethylaminodithiobenzyl) nickel (nickel dithiolene). Unlike the ambipolar semiconductors reported so far, nickel dithiolene exhibits charge-transport characteristics that are highly stable in air. Owing to this remarkable air stability, the fabrication and operation of ambipolar transistors and complementary-like circuits under ambient conditions have been achieved. Additionally, the low bandgap of nickel dithiolene permits the use of gold as an efficient ambipolar injecting electrode material. The present method is suitable for the fabrication of complex integrated circuits by using the previously reported process flowchart for state-of-the-art unipolar organic circuits.

![Image](https://example.com/image)

**Figure 6.1:** a) Absorption spectrum of a spin-coated thin film of nickel dithiolene and the molecular structure of nickel dithiolene b) schematic representation of a discrete transistor (left), formed by using a SiO₂ gate dielectric, and the generic structure of transistors employed for the construction of the integrated circuits (right), i.e., voltage inverters and ring oscillators. S and D represent the source and drain electrodes, respectively, and via the vertical interconnects that are used to connect the different metal layers.

The molecular structure of nickel dithiolene (Sensient GmbH) is shown in the inset of Fig. 6.1a. Metal dithiolene derivatives are of special interest for electronic applications because of their low bandgap and high solubility, a distinct advantage for the production of organic circuits by potentially inexpensive techniques such as inkjet printing and spin-coating. Cyclic voltammetry (CV) measurements in solution reveal that the bandgap of the nickel dithiolene employed here is on the order of 0.9 eV with the highest occupied molecular orbital
(HOMO) and lowest unoccupied molecular orbital (LUMO) at 5.2 and 4.3 eV, respectively. This bandgap value is in good agreement with the optical bandgap value obtained from the absorption spectrum of a nickel dithiolene film (Fig. 6.1a) with the absorption onset and maximum at circa 1450 and 1160 nm, respectively. Such absorption features are the result of extensive electron delocalization within the dithiolene ring system and its interaction with the d-orbitals of the central metal.\textsuperscript{15} Hence, the electronic properties of metal dithiolenes can be tailored, to a degree, simply by altering the central metal atom.\textsuperscript{17}

We have fabricated discrete OFETs using SiO\textsubscript{2} as gate dielectric and gold as source/drain electrodes (Fig. 6.1b). Fig. 6.2a shows the transfer characteristics obtained from a nickel dithiolene transistor at different bias regimes. Strong hole and electron accumulation is evident. The electron and hole mobilities (calculated in saturation),\textsuperscript{13} measured in as-prepared devices under ambient light and air, are on the order of $10^{-4}$ cm\textsuperscript{2}/(Vs). This value is typical, with the highest measured value being on the order of $10^{-3}$ cm\textsuperscript{2}/(Vs). We note, however, that in the linear regime holes are more mobile than electrons by approximately a factor of two, with typical electron mobilities in the range of $2 \times 10^{-4}$ to $8 \times 10^{-4}$ cm\textsuperscript{2}/(Vs). The apparent threshold voltages are $-5$ and $-10$ V for $n-$ and $p-$channel, respectively, with the current modulation on the order of $10^2 - 10^3$. Temperature measurements in the range of 220 – 330 K reveal a thermally activated conduction mechanism. The activation energy ($E_A$) is similar for both types of charge carriers and varies between 0.25 and 0.40 eV for high and low gate fields, respectively. By using a variable-range hopping model, developed recently for ambipolar amorphous organic transistors,\textsuperscript{18} we have been able to accurately describe ambipolar charge transport in a wide temperature range and all biasing regimes.

We emphasize that nickel dithiolene transistors are very stable, showing no noticeable degradation even after storing in ambient air (no encapsulation) for several months. Although the air stability of the $p-$channel does not come as a surprise, the $n-$channel stability is indeed surprising, as it has been observed only in very few organic materials.\textsuperscript{19–21} In this context, it is thought that the strategic fluorination\textsuperscript{21} and cyanation\textsuperscript{21} of organic molecules helps stabilize the charge carriers as well as promote close packing. Judging from the electrochem-
**Figure 6.2:** Transfer characteristics of an ambipolar transistor based on nickel dithiolene. Transistor fabrication and characterization have been performed under ambient conditions; a) room temperature transfer curves ($V_D$ is the drain voltage); b) output characteristics of a discrete device with channel length ($L$) and width ($W$) of 10 µm and 20 mm, respectively. Inset: relative position of the Fermi level of gold.

The linearity in the output characteristic data for nickel dithiolene, however, the charge carriers are not expected to be stable to $O_2$. Further work is needed to elucidate the structure-function relationship in air-stable $n$-channel organic semiconductors.

### 6.3 Complementary-like inverters and ring oscillators

Fig. 6.2b shows the output characteristics for the same transistor in hole and electron accumulation measured under ambient conditions. No significant hysteresis between forward and reverse scan is observed. For a gate voltage $V_g \leq |10|V$, the devices exhibit typical ambipolar transport characteristics with a superlinear increase in the source-drain current. The linearity in the out-
put curves, for $V_g \geq |20|$ V at low drain bias, suggests minor contact-resistance effects. We attribute this to the small energy bandgap of nickel dithiolene and the relative position of the Fermi level of gold (ca. 4.8 eV),\textsuperscript{23} situated approximately at the midgap (Fig. 6.2b, inset). This has very important consequences on the fabrication process flowchart of complementary-like circuits, since a single, high-work-function metal (e.g., gold, as in the case of unipolar architectures) is required.

Nickel dithiolene transistors have also been fabricated on flexible polymer substrates using a photoimageable polymer gate dielectric and gold source/drain electrodes under ambient conditions (Fig. 6.1b, right). Surprisingly, upon incorporation of the polymer dielectric, electron and hole mobilities were found to be lower by approximately an order of magnitude compared with SiO$_2$-based devices, while the threshold voltages remained approximately the same. By integrating a number of such transistors we have been able to fabricate complementary-like circuits. First, we fabricated voltage inverters, the building blocks of logic architectures, by integrating two transistors (Fig. 6.3a, inset). The quasi-static transfer curves of such an inverter are shown in Fig. 6.3a. A sharp inversion of the input signal is observed with a maximum voltage gain, or signal amplification, of six. We note that all inverter circuits operate in the first and third quadrant of the output-versus-input plot without any alteration in the circuit functionality - a unique characteristic of inverters based on ambipolar transistors.

The dynamic response of nickel dithiolene complementary like inverters has also been studied. Fig. 6.3b shows a schematic of the integrated inverter employed. A buffer transistor was used for matching the output impedance of the inverter to the input impedance of the measurement setup. Fig. 6.3c shows the response of the inverter (lower trace) to a sinusoidal input signal (upper trace). The output signal represents the current flowing through the buffer transistor as modulated by the voltage at the output of the inverter stage (Fig. 6.3b). As can be seen, phase inversion is achieved for input signals up to 1.1 kHz at a supply voltage of 80 V. One must note, however, that the speed of this particular circuit is limited by the high capacitive load (attributed to the large buffer transistor $L = 5 \, \mu$m, $W = 6$ mm) rather than by the intrinsic switching speed of the inverter.
6.3. Complementary-like inverters and ring oscillators

Figure 6.3: a) Quasi-static transfer characteristics of a complementary-like voltage inverter fabricated and measured in ambient conditions. Inset: complementary circuit of the voltage inverter employed b) Circuitry of the integrated inverter used for dynamic measurements. OFET 1 and OFET 2 are transistors with dimensions $L_1 = L_2 = 5 \, \mu m$, $W_1 = 100 \, \mu m$, $W_2 = 1000 \, \mu m$. As a buffer stage, a large transistor with $L = 5 \, \mu m$ and $W_1 = 6 \, mm$ has been employed.  c) Dynamic response of a complementary-like inverter to a sinusoidal input voltage at $V_{DD} = 80 V$. The upper trace is the input signal ($V_{IN}$) with a frequency of 1.1 kHz. The lower trace is the output signal current flowing through the buffer transistor, the gate of which is driven by the voltage output of the inverter stage.

Again, the circuits are stable in air and light, and capable of operating without any encapsulation even after exposure to ambient air for several months.

To test whether the complementary-like approach demonstrated here is suitable for the fabrication of more complex circuits, we have realized ring oscillators
Figure 6.4: a) Microphotograph of an inverter and a five-stage complementary-like ring oscillator fabricated side by side on a polymer substrate. The ring oscillator consists of five inverter stages and a four-stage buffer. b) Output waveform (350 Hz) of a five-stage complementary-like ring oscillator at a supply voltage of 140 V. c) Dependence of the oscillation frequency on the supply voltage and the corresponding stage delay. The solid line represents a quadratic dependence plot for comparison.

comprised of several inverter stages (Fig. 6.4a). The output characteristic of an integrated five-stage ring oscillator, fabricated and tested in air, is shown in Fig. 6.4b. The maximum oscillation frequency measured is 710 Hz, which corresponds to a stage delay ($\tau$) of $140\mu s$ ($\tau = 1/2nf$, where $n$ is the number of inverting
stages and $f$ is the measured oscillation frequency). Most importantly, the circuits exhibit a very high yield of $> 95\%$ (i.e., the fraction of functioning circuits that emerge from batch fabrication), with excellent environmental stability under ambient light and air conditions. The relatively low speed is attributed to the 15-fold mobility decrease, for holes and electrons, observed in transistors fabricated on plastic substrates using a polymer gate dielectric. Despite these low carrier mobilities, the circuits are only 15 times slower than the fastest organic complementary oscillator reported to date.\(^7\) The oscillation frequency is found to have an approximately quadratic dependence (at room temperature) on the supply voltage (Fig. 6.4c). This behavior can be understood by the nearly quadratic dependence of the pull-up and pull-down inverter currents on $V_{DD}$, as would be expected for a truly complementary ring oscillator. Work on a quantitative circuit model based on a complete description of the transistors on- and off-current, which also takes into account the nonlinearity of the gate capacitance, is currently underway.

### 6.4 Conclusion

In conclusion, dynamic operation of organic complementary-like integrated circuits based on environmentally stable ambipolar transistors has been demonstrated. Our technology combines some of the key features of unipolar and complementary logic (e.g., simple fabrication, large noise margins), which will be essential for future large-scale integration of organic transistors. Most importantly, the process gives a high circuit yield ($> 95\%$). One limitation is the low speed and the high operating voltage, but this could be improved by a combination of i) tailoring the transport properties of the semiconductor film using crystallographic engineering,\(^{24}\) ii) scaling the devices lateral dimensions,\(^{25}\) and iii) using high-mobility organic ambipolar semiconductors employing different gate dielectrics.\(^{10,12,14,26}\)
6.5 References


6.5. References


