An organic charge trapping memory transistor with bottom source and drain contacts

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We present an organic charge trapping memory transistor with lithographically defined bottom source and drain contacts. This device can be written and erased at voltages as low as 15 V. More than 500 write and erase cycles and the retention of the trapped charge over more than three months are shown, demonstrating the possibilities of this device as a reprogrammable nonvolatile organic memory element. © 2009 American Institute of Physics. [doi:10.1063/1.3223588]

Organic circuits are growing in complexity. Several hundred organic transistors are combined with high frequency diodes in transponder circuits for radio frequency identification (RFID) tags, several thousand are integrated with photodiodes in optical sensor arrays, and more than 10 000 are used to drive active-matrix organic light-emitting diode displays.^{1–4} It is expected that these and other examples will lead to electronic applications on large and flexible substrates as well as low-cost electronics. A missing electronic building block is a reliable, nonvolatile, and electrically reprogrammable memory device that can be integrated (“embedded”) with the transistors of digital logic. This would open up applications such as organic reprogrammable RFID tags or sensors capable of storing the read information. A possible candidate for such a memory element is an organic charge trapping memory transistor. This device is technologically compatible in terms of materials and device structure with logic-type organic transistors. Unfortunately, the charge trapping transistors reported so far have top source and drain electrodes patterned by shadow masks. Therefore, they cannot be integrated in circuits, neither be downscaled.

In early examples of organic charge trapping memory transistors, charges were trapped in an organic gate dielectric.^{5–7} Relatively high programming voltages and long programming times were needed. Later structures used a dielectric stack of an oxide and an organic dielectric,^{8,9} with short programming pulses $\sim 1 \mu\text{s}$ but still with relatively large programming voltages $> 50 \text{ V}$. In more complex structures the trapping centers were metal nanoparticles at or near to the gate dielectric-semiconductor interface,^{10–12} organic molecules dissolved in a polymer matrix¹³ or a stack of oxides.¹⁴ Some of these show low programming voltages, but not in combination with sufficiently long data retention. Only recently, we demonstrated that low programming voltages, short programming pulses, and a good retention can be achieved in charge trapping memory transistors with a simple dielectric stack of an oxide and an organic dielectric, still with top source and drain contacts.¹⁵

Building on those results, we realized now an organic charge trapping memory transistor with a stacked dielectric

structure and lithographically defined bottom source and drain contacts. We show that these devices can be written and erased with short pulses at low programming voltages and that data is retained over more than 3 months. Moreover, several hundred write and erase cycles are demonstrated. This demonstrates the possibilities of this device as a reprogrammable and embedded nonvolatile memory element.

The transistors in this study have a bottom gate electrode and bottom source and drain electrodes, as depicted in Fig. 1. The substrate is a highly *n*-doped Si wafer with 20 nm of thermally grown SiO₂ on top. The highly *n*-doped Si serves as the gate electrode. Gold source and drain electrodes are patterned on top of the SiO₂ by a lithographic process. Next, these samples are dipped in a 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol solution in ethanol to form a monolayer of this thiol on top of the Au electrodes (Fig. 1). After rinsing the samples with ethanol, a 4 nm thick layer of poly(alpha-methylstyrene) (PαMS) is deposited by spin coating a 0.1 wt % PαMS solution in toluene at 4000 rpm. In this process, the PαMS is repelled from the thiolated metal contacts, and is confined spontaneously to the channel region of the transistor.¹⁶ The stack of SiO₂ and PαMS forms the gate dielectric. As a last step, a 40 nm thick layer of pentacene is deposited by organic molecular beam deposition ($p \sim 10^{-8} \text{ Torr}$). The deposition rate and the substrate temperature during pentacene deposition are 0.25 Å/s and 68 °C, respectively. The transistors have channel lengths $L = 10 \mu\text{m}$ and channel width $W = 1000 \mu\text{m}$. The initial hole mobility extracted from the linear regime, $\mu_{h,\text{init}}$ and the ini-

FIG. 1. (Color online) Schematic view of a bottom contact memory transistor, together with the chemical structure of the heptadecafluoro-1-decanethiol, employed on the source and drain electrodes.

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FIG. 2. (Color online) V_{on-} , V_{on+} , and ΔV_{on} as a function of $|V_{GS,prog}|$ for $t_{prog}=1.5$ ms. The inset shows the hole mobility in the two memory states, as a function of $|V_{GS,prog}|$ for $t_{prog}=1.5$ ms.

tial threshold voltage $V_{T,init}$ are typically ~ 0.3 $\text{cm}^2/(\text{V s})$ and ~ -0.3 V.

Electrical data are obtained using two computer controlled Keithley 2602 units in a darkened nitrogen glovebox. Samples were not subjected to air. The measurement protocol is described elsewhere but briefly repeated here.¹⁵ First, the initial characteristics were measured to determine the initial turn-on voltage, $V_{on,init}$, of the device. The turn-on voltage V_{on} is defined as the gate-source voltage V_{GS} at which the drain current I_D reaches 100 pA. Then, the device is subjected to a write pulse with pulse length t_{prog} and a negative programming voltage $-V_{GS,prog}$. The erase pulse has the same length t_{prog} , as the write pulse, and a positive programming voltage $V_{GS,prog}$, equal but opposite to the programming voltage of the write pulse. The drain-source voltage during programming, $V_{DS,prog}$, is always kept at 0 V. After a pulse, a small part of the transfer characteristics is measured to determine V_{on} . We denote by V_{on-} the turn-on voltage after a negative write pulse, and V_{on+} is the turn-on voltage after a positive erase pulse. ΔV_{on} is defined as the difference between V_{on+} and V_{on-} . These measurement steps can then be repeated for different $|V_{GS,prog}|$.

In Fig. 2, V_{on-} , V_{on+} , and ΔV_{on} are plotted as a function of $|V_{GS,prog}|$, with $|V_{GS,prog}|$ increasing from 0 to 20 V in steps of 1 V. The observed shift in turn-on voltage at high programming voltages can be explained by trapping of holes and electrons in the gate dielectric stack.^{8,15} At low programming voltages ($|V_{GS,prog}| < 10$ V), $V_{on-} = V_{on+} = V_{on,init}$, and $\Delta V_{on} = 0$ V. At these voltages, the electric field over the P α MS is too low for the holes and electrons to be injected into the dielectric stack and as a result no charges are trapped. For values of $|V_{GS,prog}|$ between 10 and 14 V, $V_{on-} \approx V_{on+} < V_{on,init}$. Holes can tunnel into the dielectric stack during the negative write pulse, resulting in a more negative V_{on-} . But these trapped holes cannot be removed, nor be overwritten by electrons during the positive erase pulse.¹⁵ From 14 V on, the transistor can be programmed between two distinct states with different V_{on} . During a negative write pulse, holes can be trapped in the gate dielectric leading to a more negative V_{on-} . A positive erase pulse, on the other hand, leads to the trapping of electrons, overwriting the trapped holes and re-

sulting in a more positive V_{on+} . The higher $|V_{GS,prog}|$, the more charges can be trapped and the higher ΔV_{on} . After $|V_{GS,prog}|$ reaches 20 V, we repeat the measurement procedure but with $|V_{GS,prog}|$ decreasing from 20 to 0 V. The measured V_{on+} , V_{on-} , and ΔV_{on} lay on top of the first scan for $|V_{GS,prog}| > 14$ V, illustrating the reproducibility of the write and erase mechanism. Only at the end of the measurement ($|V_{GS,prog}| < 14$ V), V_{on-} and V_{on+} end up at a voltage slightly more negative than $V_{on,init}$ indicating that some net positive charge remains trapped.

Interestingly, the trapping of both holes and electrons also affects the transistor's hole mobility. We show in the inset in Fig. 2 the hole mobility extracted in the linear regime of the transistor, after the negative write (μ_-) and positive erase pulses (μ_+). Two trends in μ_+ and μ_- can be noticed when $|V_{GS,prog}|$ is increased from 0 to 20 V and decreased back to 0 V. First, when $|V_{GS,prog}|$ increases above 14 V, μ_+ becomes smaller than μ_- . This can be related to the trapping of electrons in the dielectric. Calhoun *et al.*¹⁷ reported that electrons trapped in the dielectric reduce the hole mobility in the channel, while holes trapped in the dielectric do not. This is again an indication that from 14 V on, electrons and holes are indeed alternately trapped in the dielectric stack. Second, there is an overall decrease in the hole mobility as a result of the repeated pulses at high $|V_{GS,prog}|$ [μ_+ and μ_- are reduced from 0.28 to 0.23 $\text{cm}^2/(\text{V s})$]. It is not clear if this overall decrease is mainly due to the trapping of either holes or electrons and the accompanying damage to the pentacene/P α MS interface, but it can be reduced by limiting $|V_{GS,prog}|$.

To open the memory window at low $|V_{GS,prog}|$, the trapping of both holes and electrons is needed.¹⁵ At $|V_{GS,prog}| = 15$ V, ΔV_{on} is almost 2 V corresponding to a ratio of the drain currents in the two memory states, I_{D+}/I_{D-} , of more than 200 (I_{D+} and I_{D-} measured at $V_{GS,sense} = -1.5$ V and $V_{DS,sense} = -0.02$ V).

Figure 3(a) shows the evolution of V_{on-} , V_{on+} , and ΔV_{on} with the increasing number of cycles (one cycle being a combination of a write and an erase pulse). After more than 500 cycles at $|V_{GS,prog}| = 15$ V and $t_{prog} = 1.5$ ms, ΔV_{on} decreases from 1.9 to 1.4 V. As important is the evolution of I_{D+}/I_{D-} , depicted in Fig. 3(b) (I_{D+} was measured at $V_{GS,sense} = -1.5$ V and $V_{DS,sense} = -0.02$ V. I_{D-} was taken fixed at 10 pA to exclude variations in I_{D+}/I_{D-} due to the noise in the cutoff current of the transistor). As the inset of Fig. 3(b) shows, the variations in I_{D+}/I_{D-} are caused by a slight shift in V_{on+} and V_{on-} (I_{D+}/I_{D-} rises) and an overall decrease in the hole mobility (I_{D+}/I_{D-} decreases). After more than 500 cycles, $I_{D+}/I_{D-} > 130$, and the device still works as a memory transistor with two distinct states.

The retention of the trapped charges is another important figure of merit, shown in Fig. 4. After a write pulse with $-V_{GS,prog} = -20$ V and $t_{prog} = 1.5$ ms, V_{on} was measured at different time intervals. The same was done on another device on the same sample after an erase pulse with $V_{GS,prog} = 20$ V and $t_{prog} = 1.5$ ms. In between the measurements, the sample was left in a darkened nitrogen glovebox, without applying any voltages to the electrodes. Each data point is the average of measurements on at least two different devices. At this $|V_{GS,prog}|$, the retention of both the trapped holes and the trapped electrons can be tracked. After 3 months, all trapped electrons are lost and V_{on+} is reduced to 0

FIG. 3. (Color online) (a) V_{on-} , V_{on+} , and ΔV_{on} as a function of the number of cycles for $t_{prog} = 1.5$ ms and $|V_{GS,prog}| = 15$ V. (b) I_{D+}/I_{D-} as a function of the number of cycles for $t_{prog} = 1.5$ ms and $|V_{GS,prog}| = 15$ V. I_D was measured at $V_{GS,sense} = -1.5$ V and $V_{DS,sense} = -0.02$ V. The inset shows the transfer characteristics in the two memory states after different numbers of cycles.

V_{on-} on the other hand, tends to saturate toward -2 V, indicating that the holes are trapped in a trap distribution that contains also deep traps. These deeply trapped holes result in a good retention but, as we showed in Fig. 2, can be over-

FIG. 4. (Color online) Retention measurement for a bottom contact memory transistor. The first point of the V_{on-} curve is reached after a write pulse with $-V_{GS,prog} = -20$ V and $t_{prog} = 1.5$ ms. The first point of the V_{on+} curve is reached after an erase pulse with $V_{GS,prog} = 20$ V and $t_{prog} = 1.5$ ms.

written by electrons during an erase pulse with $V_{GS,prog} > 14$ V. The good retention of the trapped holes confirms the possibility to use this device as a nonvolatile memory element.

In summary, we realized an organic charge trapping memory transistor with bottom source and drain contacts. Holes can be trapped in the gate dielectric during a write pulse of 1.5 ms at -15 V. These trapped holes can be erased by overwriting them by electrons with a pulse of 1.5 ms at 15 V. More than 500 cycles have been measured with an I_{D+}/I_{D-} systematically larger than 100 and the retention of trapped holes was shown to be longer than 3 months. The compatibility of the device fabrication and structure with that of logic-type transistors and its promising figures of merit indicate that this device type is an interesting candidate for nonvolatile memory embedded with plastic logic.

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