All-Organic Permanent Memory Transistor Using an Amorphous, Spin-Cast Ferroelectric-like Gate Insulator

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All-Organic Permanent Memory Transistor Using an Amorphous, Spin-Cast Ferroelectric-like Gate Insulator**

By *Raoul Schroeder,* *Leszek A. Majewski*, and *Martin Grell*

Organic field-effect transistors (OFETs) are one of the current hot topics in the materials science and materials chemistry field.[1–3] Of similar performance, but cheaper than amorphous silicon,[4] OFETs are aimed at disposable, mobile, flexible low-duty applications. Memory elements for OFET applications, such as display driver logic[5,6] or radio frequency identification (RFID) tags are,[7,8] however, limited: capacitor elements for active matrix display logic are volatile and refreshment is current-intensive. First attempts at non-volatile organic memories involve electrets[9] and capacitors integrated in the gate electrode ("floating gates").[10] These transistor memories, however, have to be charged at high voltages for seconds, and the memory is not truly permanent (timescale: minutes). Inorganic permanent single transistor memories using ferroelectrics[11–15] overcome this for high-quality inorganic electronics, but are not suitable for OFETs due to poor performance of organic semiconductors on them,[16] cost, and incompatibility with flexible substrates, an important advantage of organic transistors.[17,18]

In this communication, we present the "FerrOFET", an entirely organic memory device. In what results in a huge simplification of the production process, we rely on the discovery by Murata et al.[19] of amorphous polymers that exhibit ferroelectric-like properties. Surprisingly, this class of polymers, a cheap, commercially available nylon poly(*m*-xylylene adipamide) (MXD6) (see Fig. 1a, with *n* = 4), is ferroelectric-like in its amorphous state, not in its crystalline state.[20] Ferroelectric-like means that the displacement versus electric field (*D*–*E*) hysteresis exhibits the same shape as typical ferroelectric materials but, as an amorphous material, it does not exhibit the thermodynamic phase or crystalline structure associated with ferroelectricity. The polymer does not exhibit a Curie temperature, above which the remanent polarization ceases; instead ferroelectric-like behavior is only observed up
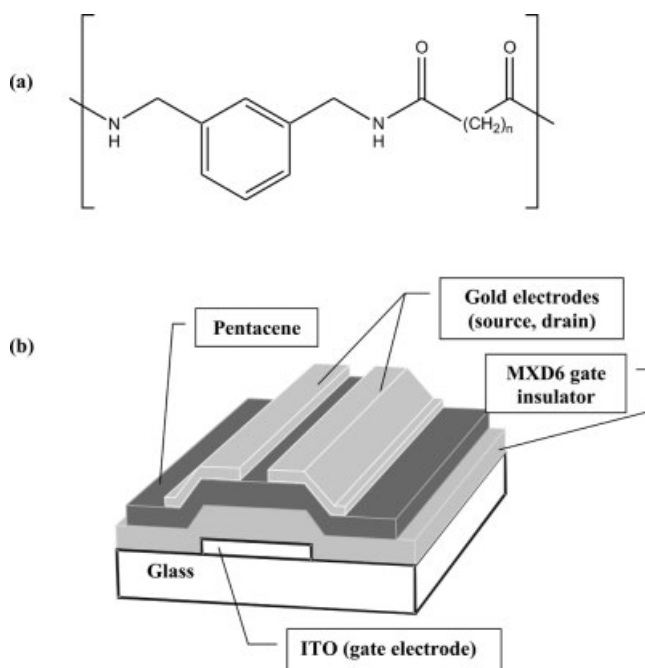
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Figure 1. a) Chemical structure of MXD6. b) Structure of the "FerrOFET" device.

to the glass transition temperature. The mechanism is not entirely clear, but it is conceivable that, in the amorphous state, the intermolecular hydrogen bonds between amide and carboxyl groups are able to align in response to an external field, whereas crystallization quenches the alignment. Research on the material itself continues,[21] but has never resulted in any application until now.

Murata et al. reported on the ferroelectric-like properties of MXD6 drawn from a melt (thickness 20–45 μm), but neither the process nor the insulator thickness are compatible with organic transistor technologies. We therefore successfully verified first that a thin film spun from solution retains its ferroelectric-like behavior. The use of MXD6 for transistor memories is an enormous simplification of the production technology compared to their inorganic counterparts, as there are no lattice constants of the ferroelectric material and the semiconductor to be matched. It is very simple to build the FerrOFET, and a schematic diagram of the prototype device is shown in Figure 1b.

The terminology of ferroelectric transistors is extended from that of regular transistors, as the functionality is somewhat different. The three most important characteristics are defined as follows. The "memory window" signifies the difference of the threshold voltages between the sweeps in the negative and positive voltage directions. This value is significant for the voltage difference necessary to turn the memory transistor "on" and "off", and in inorganic ferroelectric transistors this value is usually 5–10 V.[13–15] The "memory ratio" or "channel resistance modulation" describes the difference in current when no gate voltage is applied, depending on how the ferroelectric memory was poled beforehand. It is not to be confused with a regular transistor "on"/"off" ratio, which needs to be very high to minimize capacitor discharge through the channel. Low reported values for memory ratios are on the order of five,[13,14] whereas the highest reported value we are aware of was 1000 initially and 100 after 1 s.[15] Finally, it is important to know how long the memory is retained, and typical values are a 10 % or 20 % loss of the "on" current over a few hours.

In Figure 2, the transfer characteristics of the FerrOFET memory transistor are shown, for a source-to-drain voltage of –5 V, and it shows that there is a clearly visible hysteresis between the two source–drain currents for the gate voltage sweep in the negative and positive directions. Most importantly, the memory writing process in the FerrOFET is just like turning on a regular transistor, but subsequently the FerrOFET can be read without an applied gate voltage. This is in contrast to other "non-volatile" electret transistors, which require charging with a high voltage of opposite polarity compared to normal operation (i.e., positive voltages for p-type transistors) and also necessitate a gate voltage to read the written state.[9]

Figure 2a shows a sweep at four seconds per data point in a linear–logarithmic plot. The "on" current is 40 nA, after poling the gate to –20 V. The "off" current appeared to be 0.2 nA, which is equal to the noise floor of the Keithley 2400
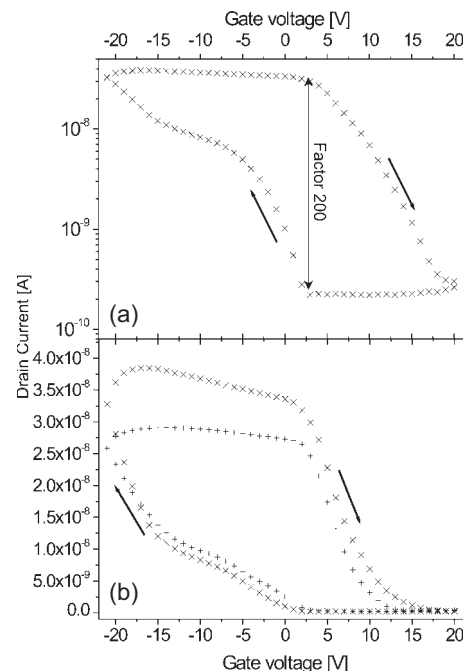

Figure 2. a) Transfer characteristic of an MXD6/pentacene "FerrOFET" with an applied drain voltage of –5 V. The memory window, the difference between the threshold voltages on the up and down sweeps, is 20 V wide, and the "memory ratio" around 0 V at the gate is a factor of 200. The measurement sweep rate is four seconds per point (or 0.25 V/s). b) To investigate the influence of the sweep rate, the same device was measured with two different sweep rates. The data points shown as crosses are identical to the data in (a) and were measured at a rate of four seconds per point (or 0.25 V/s). The data points shown as plus signs were collected at two seconds per point (or 0.50 V/s).

source measurement unit (see Experimental section), and was reached at a gate voltage of +15 V. This corresponds to a memory ratio of at least 200, which is a very competitive value even when compared to inorganic ferroelectric transistors. Since we cannot determine the actual "off" current with the Keithley 2400s, the factor of 200 between the "on" and "off" currents is just the lower limit. Already, compared to our first prototype devices with memory ratios of around 5, a memory ratio of 200 is a big step forward, and the actual theoretical limit is greater than 10^5 (due to MXD6's high remanent polarization of 60 mC/cm^2, see the literature[19]). Therefore, further improvement in the future is most definitely achievable. Also, it should be noted that while the difference in poling voltage from completely "off" to completely "on" is 35 V, the actual memory window is defined as the difference between the threshold voltage in the "up" and "down" sweeps of the gate voltage. This memory window is 15 to 20 V for this FerrOFET device and can be adjusted by changing the thickness of the gate insulators. This value is somewhat higher than the memory window in inorganic ferroelectric transistors, where memory windows are typically on the order of 5 V.

The gate leakage currents in general are below the resolution of the Keithley 2400 (0.1 nA) and are presumably close to zero; however, there is an apparent transient leakage cur-

rent when switching from reading ($V_G = 0$ V) to writing mode ($V_G = \pm 20$ V). This, in fact, is not a leakage current, but a transient displacement current ($j = dD/dt$) resulting from the change of polarization of the ferroelectric. The charging current is 1 nA, and runs for several hundred milliseconds. The charge deposited in the ferroelectric is therefore less than 1 nC. Thus, the electrical displacement deposited in an area the size of the source electrode, 0.04 cm^2, is 5–10 nC/cm^2. This polarization is lower than the remanent polarization, 6 μC/cm^2, reported by Murata et al.,[19] indicating that further improvements to the deposition of the ferroelectric-like insulator are possible, and will further enhance the device performance.

In Figure 2b, we show the memory hysteresis when measured at different scan speeds, the crosses denoting measurements at a rate of 0.25 V/s (identical data to Fig. 2a), the plusses showing measurements at a rate of 0.50 V/s. The two curves are largely identical, except for a slightly higher "on" current for the slower speed. The difference, however, is insignificant, and is most likely due to the fact that the fast sweep was the second sweep measured in the lifetime of the transistor, whereas the operation mode only fully stabilizes after five complete hysteresis sweeps. The comparison of the data at two different sweep states demonstrates that the memory of the transistor is not due to charge build-up, but a genuine remanent polarization that does not depend on the write or read speeds.

Finally, we tested the memory retention lifetime of the FerrOFET under permanent read conditions (Fig. 3) and intermittent read conditions (Fig. 4). It was mentioned above that the
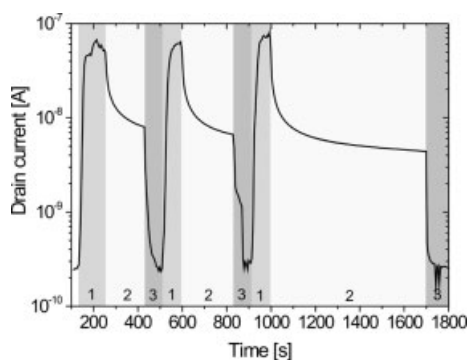

Figure 3. Ferroelectric memory stability under constant read operation. Sections labeled 1: writing of state 1 ($V_G = -20$ V). Sections labeled 2: read ($V_G = 0$ V). Sections labeled 3: writing of state 0 ($V_G = +20$ V). While an initial factor of 4 in current is lost quickly, a remaining memory ratio of 50 is held for much longer periods.

surface charge deposited due to gate sweep is a maximum of 0.5–1 nC. Looking at the read cycles in Figure 3 reveals that the average current running through the device is 8–10 nA for 700 s. This corresponds to a charge of up to 7 μC crossing the channel, exceeding the charge deposited while poling the ferroelectric by four orders of magnitude. This is definite proof that the memory effect in the FerrOFET does in fact stem from a remanent polarization that induces accumulation in
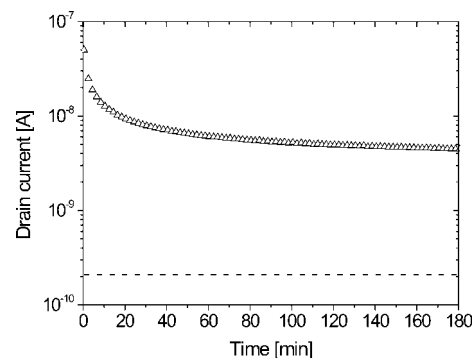

Figure 4. Ferroelectric memory stability under intermittent read operation, i.e., one read operation (0.5 s) every 120 s. The off current of the "FerrOFET" is shown for comparison (dashed line). This is a much more realistic scenario of the application usage of the "FerrOFET", and extends the retention of the memory over several hours for the prototype device.

the channel. The FerrOFET memory transistor loses about a factor of four of the current very quickly, and then maintains the remaining factor of 50 over the "off" current during extended read periods. This behavior is similarly observed for inorganic ferroelectric transistors.[15]

However, in Figure 4, where the device was poled into the "on" state, and only read for 0.5 s every 120 s, the memory loss over 3 h is around 20 %, after the initial drop, which has been reported for inorganic ferroelectric transistors as well.[15] Therefore, it appears that the strongest factor determining the depolarization of the ferroelectric gate insulator is the current running through the channel, and/or some leakage of the ferroelectric insulator below our resolution limit. For a memory device that was to be read incessantly (an extremely rare device application), this could mean that the memory may need to be refreshed every hour, which is still orders of magnitude slower than the refresh cycle of transistor/capacitor memory devices, where the refresh cycle is usual tens of milliseconds. A memory device that is only rarely read retains the memory for much longer time periods.

In conclusion, we have presented OFET transistors with gate insulators based on the amorphous, ferroelectric-like, transparent, and easy to process material MXD6. The single-transistor, permanent memory devices (FerrOFETs) built in this fashion feature very competitive device properties compared to inorganic ferroelectric transistors, yet are substantially easier and cheaper to fabricate. Through the analysis of the FerrOFET with different scan speeds, as well as memory retention stability during laboratory-type incessant read tests and short reads every 2 min, we were able to demonstrate clearly that the memory effect observed in fact occurs because of the remanent polarization of the ferroelectric gate insulator MXD6. The FerrOFET presented here already has all the required characteristics for possible applications such as RFID tags and low power mobile memories: a memory window of 20 V, a reasonable operating voltage for current OFET applications, a memory ratio of at least 200 for "on" to "off" currents, and long memory retention times.

COMMUNICATIONS

Experimental

Poly(*m*-xylylene adipamide) (MXD6) was obtained from the Mitsubishi Gas Company. It was dissolved as-received in *m*-cresol (99.3 % purity), obtained from Aldrich, in a concentration of 35 g/L. It was subsequently spun onto a glass/ITO (indium tin oxide) substrate. Pentacene, acquired from Aldrich, was thermally evaporated as-received at a pressure of 8×10^{-7} torr at a rate of 3 Å/s, from a quartz crucible in a tungsten heater basket. Gold was formed as a top layer electrode through shadow masks, with an electrode area of 2 mm × 2 mm for both source and drain with a distance of 25–80 μm in between, the channel length. Gold was evaporated at a speed of 2 Å/s.

The fabricated devices were measured using two Keithley 2400 source measure units to provide the gate and drain voltages, as well as measuring source–drain currents and source–gate leakage. Keithley 2400 units have a maximum resolution of 5×10^{-11} A. Also, they show a DC current offset of up to $\pm 4 \times 10^{-10}$ A, in our case -1.2×10^{-10} A for the instrument measuring the gate leakage current, and -2.3×10^{-10} A for the instrument measuring the drain current.

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Reversible Photoregulation of the Electrical Conductivity of Spiropyran-Doped Polyaniline for Information Recording and Nondestructive Processing**

By *Xuefeng Guo, Deqing Zhang,* Gui Yu, Meixiang Wan, Junchao Li, Yunqi Liu,* and *Daoben Zhu**

Molecular-based materials with photoresponsive physical (e.g., electrical and magnetic) properties are very important for the development of molecular electronics and optoelectronics. In recent years, several examples of photo-modulation of the magnetic properties of molecular magnets have been described,[1] although photoregulation of the electrical conductivity of organic conducting materials has hardly been reported.[2] We report here for the first time the reversible photoregulation of the electrical conductivity of a polyaniline (PANI) thin-film doped with spiropyran (SP).

It is noteworthy that the electrical conductivity of polyaniline depends not only on the level of oxidation but also on the degree of protonation.[3] The reversible interconversion of the "base form" and the "salt form" can be achieved by employing the principle of acid/base (doping/de-doping) chemistry, enabling control over the electrical conductivity. It has been reported[4] that the "base form" of polyaniline can be transformed into the corresponding "salt form" in the presence of a photoacid generator upon irradiation. However, this photo-induced proton-doping process was irreversible.

Interconversion among the three states of spiropyran (the closed form SP, the open form ME, and the protonated open form MEH; see Scheme 1) accompanies the reversible uptake and release of protons upon UV or visible-light irradiation, as shown in Scheme 1.[5] If this light-regulated reversible uptake and release of protons by spiropyran is combined with the unique property of polyaniline mentioned above (dependence of its conductivity on the level of protonation), then the electrical conductivity of polyaniline could be reversibly photo-controlled (Scheme 1). In other words, if polyaniline and spir-

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