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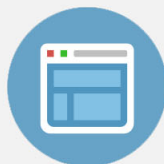
Low-voltage polymer field-effect transistors for nonvolatile memories

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We demonstrate organic nonvolatile memories based on transistors, made from spin-coated polymers, that have programming voltages of 15 V and good data retention capabilities. The low-voltage programmable ferroelectric field-effect transistors were obtained by an optimized ferroelectric polymer deposition method using cyclohexanone as a solvent from which films can be obtained that are thin, smooth and defect free. The data retention characteristics were measured for 3 h under constant read conditions. Extrapolation predicts that the data retention capability exceeds 10 years. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2132062]

In recent years there has been a surge in research efforts to make organic nonvolatile memories.[1–8] One type of memory element under investigation is the organic transistor with a functionalized polymer gate dielectric.[4–8] The main benefit of this device is that it should integrate easily into an existing technology based on organic transistors because of the similar device architecture. Memory functionality is obtained by the bistable polarization of a polymer ferroelectric or electret gate dielectric, which remanently attenuates the charge density in the semiconductor channel. We have recently demonstrated a solution-processed ferroelectric field-effect (FeFET) based on the combination of poly(vinylidene fluoride/trifluoroethylene) (PVDF/TrFE) as the ferroelectric polymer and a poly(*p*-phenylene vinylene) derivative as the semiconducting material.[4] Comparison to other recent reports shows that only the P(VDF/TrFE)-based device has a short programming time of 1 ms that is in agreement with the speed of organic circuits. Singh *et al.* found that their electret-based devices are charged in about 40 s.[7] Schroeder *et al.* have not reported a programming time for their ferroelectric-like MXD6 nylon-based devices,[6] but the switching time of nylons is known to be longer, by four orders of magnitude, than that of P(VDF/TrFE) at the same applied electric field.[9] P(VDF/TrFE) is therefore the best materials choice. However, a major shortcoming of the reported FeFETs is that the programming voltage, estimated from the drain current saturation points in the transfer curve measurement, amounts to 50 V or more,[4,5] while in organic FETs and invertors the operating voltages are typically 10–20 V.[10] Here we report on polymer FeFETs that have a programming voltage of 15 V and a good data retention capability. These measurements were enabled by the optimized processing and deposition of the ferroelectric.

Because ferroelectrics switch at a specific electric field called the coercive field, low-voltage operational FeFETs can be obtained by using a thin ferroelectric gate dielectric. However, in order to obtain high quality thin films one needs to optimize the deposition method. All previous reports on spin-coated P(VDF/TrFE) thin films were done with dimethylformamide (DMF) or 2-butanone (MEK) as a solvent, most likely due to the high solubility of 100 mg/ml or more. DMF, however, is carcinogenic and hydroscopic and therefore has a limited applicability.[11] MEK has a low viscosity and a high vapor pressure, which is detrimental to its film forming characteristics. Consequently, our attempts to make thin film capacitors with MEK often resulted in a short circuit between the top and bottom electrodes. This happens especially with gold electrodes, which are typically used for source-drain electrodes in organic FETs, because evaporation deposition can lead to diffusion of the metal into the polymer. This probably explains the fact that most reports on P(VDF/TrFE) thin film capacitors use Al or Ni top electrodes,[12] because these metals chemically react with fluoropolymers,[13,14] which prevents diffusion. We solved this processing problem and obtained high quality thin films using cyclohexanone as a solvent, which has a higher viscosity than either MEK or DMF. Other more viscous solvents such as 4-hydroxy-4-methyl-2-pentanone were tested as well, but these form an unprocessable, gel-like solution at higher concentrations. Cyclohexanone on the other hand, forms clear solutions at high concentrations. As a result, we obtained a viscous solution that is especially suitable for spin coating. The kinematic viscosity, measured with an Ubbelohde glass capillary viscometer at 293 K, is 73 mm^2/s for a 50 mg/ml concentration. This value is comparable to that of certain motor oils.

To demonstrate the high quality of the thin films spin coated from this solution, we prepared capacitors. Bottom electrodes were deposited onto clean glass substrates by shadow mask evaporation of a thin chromium adhesion layer and gold. Subsequently, poly(vinylidene fluoride/ trifluoroethylene) 65/35 mol % random copolymer (Solvay Duphar, Belgium) was applied by spin coating 50 mg/ml cyclohexanone solutions (dissolved and filtered at 60 °C) at 4000 rpm. The films were annealed in a vacuum oven at 138 °C to enhance the crystallinity. The layer thickness, determined using a Dektak profilometer, was 200 nm. Capacitor devices with an area of 1 mm^2 were completed by shadow mask evaporation of a second gold layer. Dielectric displacement measurements performed at 10 Hz yielded a remanent polarization of 74 mC/m^2 and a coercive field of 50 MV/m. These values are identical to those of the bulk material.[15] Figure 1 presents the current-voltage characteris-

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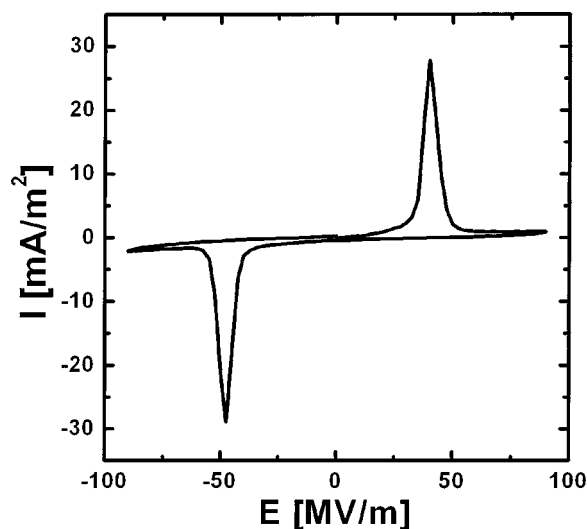[a]Author to whom correspondence should be addressed; electronic mail: r.c.g.naber@rug.nl

FIG. 1. Current-voltage characteristics of a capacitor with a ferroelectric layer thickness of 200 nm. The voltage was scanned to ±18 V at a rate of 1 V/s.

FIG. 3. Ferroelectric field-effect transistor transfer curve (filled circles) and the gate current (line) obtained with a gate insulator layer similar to that in Fig. 1 and a regioregular poly(3-hexylthiophene) semiconductor material. The drain voltage V_D, semiconductor channel width W and length L are included. The device was previously programmed into the off state.

tic of the capacitors as measured with a Keithley 2400 SourceMeter, which shows that the leakage current at an electric field of 90 MV/m has a low value of 2 mA/m^2. The current peaks in the measurement are due to the ferroelectric polarization. Figure 2 presents atomic force microscopy (AFM) measurements on the films after annealing. Especially the phase image clearly shows that the films consist of crystallites that are interconnected similar to a maze, with a width in the range of 60–120 nm. The root-mean-square surface roughness is 5 nm, which is a typical value for a semi-crystalline polymer.

Having demonstrated these ferroelectric polymer thin films, we proceed with FeFETs. In the transfer curve measurement, the drain voltage is preferably small so that it will not affect the polarization state of the ferroelectric. Measurements performed with a drain voltage that is half the coercive field of the ferroelectric layer gave transfer curves which are askew due to this effect. In order to avoid this but still obtain a high drain current signal with a small drain voltage, we use a semiconducting polymer with a high mobility, namely regioregular poly(3-hexylthiophene) (rr-P3HT). This polymer crystallizes, which enhances the molecular orbital overlap and forms a high mobility phase.[16]

The fabrication of the FeFETs was kept identical to the capacitors, except that the top electrode consists of gold
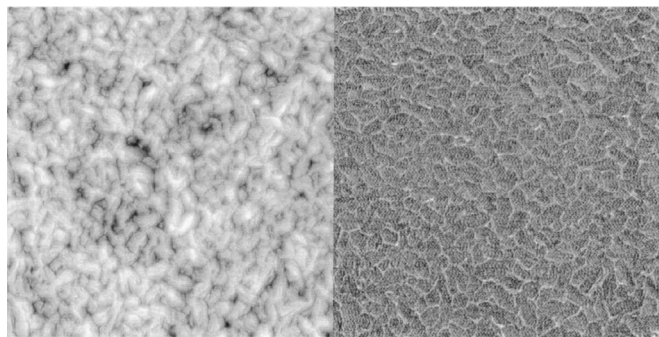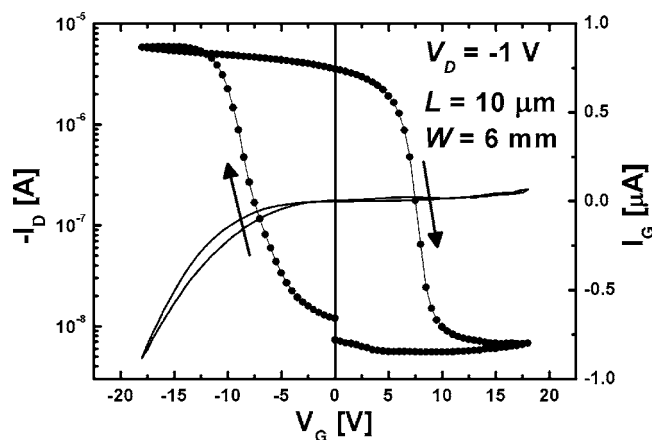

FIG. 2. AFM measurement on an annealed P(VDF/TrFE) layer with a thickness of 200 nm. The area size is 2 by 2 μm^2 with on the left the topography (20 nm gray scale range) and on the right the phase response of the same area (7° gray scale range).

source-drain electrodes. These were deposited with shadow mask evaporation, using a wire to create the channel. The typical source-drain spacing amounts to 10 μm. Regioregular poly(3-hexylthiophene) (Rieke Metals, Inc.; electronic grade; 98.5% regioregular) was purified after purchase by the following procedure. It was dissolved in distilled toluene, de-doped with hydrazine at 60 °C and precipitated in methanol. The fraction collected was Soxhlet extracted for at least 64 h with methanol, *n*-hexane, CH_2Cl_2 and finally with $CHCl_3$. The chloroform fraction was precipitated in methanol, dried under vacuum and stored in the glovebox under a N_2 atmosphere. The purified semiconducting polymer was dissolved in chloroform and spin coated onto the FeFET in a N_2 filled glovebox. These devices were annealed a second time in a vacuum oven at 138 °C to raise the crystallinity of the rr-P3HT. Experiments without annealing a second time resulted in a lowering of the mobility which indicates that the annealing enhances the semiconductor crystallinity. Figure 3 presents a transfer curve measurement performed in dark and vacuum using a Keithley 4200 semiconductor analyzer. The device operates in the linear regime because the gate voltage far exceeds the drain voltage. The field-effect mobility derived from the slope at zero gate bias, using a measured insulator capacitance per unit area of 44 nF/cm^2, is 8×10^{-3} cm^2/V s, which is a typical value for this polymer.[16] The gate current at -18 V that can be expected based on the leakage current measurement in Fig. 1 and the total surface area of the transistor is 4 nA, but it is higher than that in Fig. 3 because in accumulation the unpatterned semiconductor layer acts as a leakage path between the source-drain and gate electrodes.

The industrial standard for data retention of any nonvolatile memory device is 10 years. Retention times up to 1 week have been measured on organic memory transistors, but these measurements were under floating gate conditions.[4,6,7] This slows down retention loss because the charges in the gate electrode are not free to exit the device. Unni *et al.* performed their retention measurement in non-floating conditions, but the drain voltage level of -40 V is much higher than necessary and therefore does not represent the nondestructive readout operation of FeFETs.[5] For inorganic FeFETs, the primary mechanisms for retention loss are
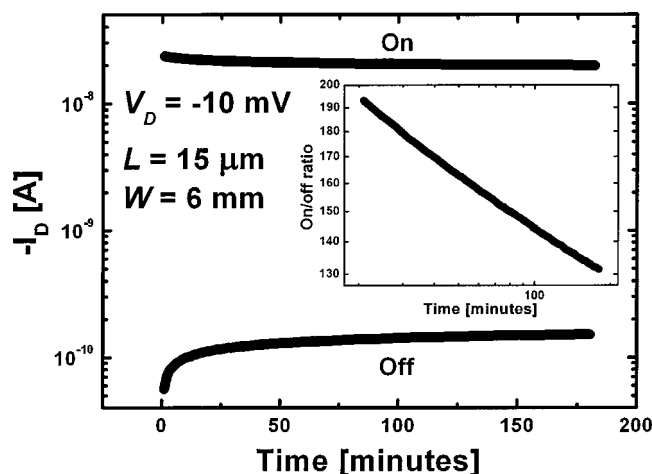
FIG. 4. Data retention measurement of the on- and off-state drain current of an FeFET with a gate insulator layer similar to that in Fig. 1, obtained with a continuous drain voltage and with the gate and source electrodes connected to 0 V. The inset shows the drain current on/off ratio on a double logarithmic scale.

depolarization and charge injection into the ferroelectric.[17] For P(VDF/TrFE) the latter mechanism is less probable because it is a wide band gap insulator unlike most inorganic ferroelectrics. The depolarization field is caused by the field-effect band bending in the semiconductor and it increases with decreasing ferroelectric layer thickness.[18] It is therefore especially relevant to measure the depolarization dynamics with the present thin films. We measure the data retention with all the electrodes near 0 V, so that the externally applied fields are low and the device is free to depolarize. This is also the standard method of obtaining the retention time for inorganic FeFETs.[19] Figure 4 presents the results obtained after sweeping the gate voltage to ±18 V and shortly connecting the three terminals together to remove any capacitive charge. The drain voltage was lowered by a factor of 100 with respect to Fig. 3 because the gate current is much lower at zero gate bias and the drain current therefore exceeds the gate current even at such a low drain voltage. The measurement in Fig. 4 is consistent with Fig. 3, since the drain currents are also decreased by a factor of 100. The on and off currents change only slightly in 3 h. The reprogrammed devices start at the initial current levels again, which indicates that they change due to depolarization. The inset in Fig. 4 shows that the drain current on/off ratio decreases linearly on a logarithmic time scale. Using the slope, the predicted retention time for an on/off ratio higher than 10 is 10^8 min, which exceeds the 10 years requirement.

We note that recently all-polymer FeFETs have also been realized, with solution-processed poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes.[20] The retention was shown to be limited. This was attributed to the chemical impurities that are introduced by the particular lithographic process that was used to pattern these polymer electrodes.[21] Here we show that cleanly prepared devices without chemical impurities have a good retention capability.

In summary, we demonstrated a polymer nonvolatile memory device with a programming voltage of 15 V, which is compatible with voltages used in integrated circuits based on organic semiconductors. This operation voltage is achieved by optimizing the ferroelectric layer deposition technique using cyclohexanone as a solvent, which results in thin, smooth and defect-free ferroelectric films.

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