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Organic Nonvolatile Memory Devices Based on Ferroelectricity

By Ronald C. G. Naber,* Kamal Asadi, Paul W. M. Blom, Dago M. de Leeuw, and Bert de Boer

A memory functionality is a prerequisite for many applications of electronic devices. Organic nonvolatile memory devices based on ferroelectricity are a promising approach toward the development of a low-cost memory technology. In this Review Article we discuss the latest developments in this area with a focus on three of the most important device concepts: ferroelectric capacitors, field-effect transistors, and diodes. Integration of these devices into larger memory arrays is also discussed.

1. Introduction

The ability to store information is essential to many of the envisioned applications of organic electronics. RFID tags, e.g., need to be able to send and receive stored information that is communicated by means of a radio signal.^[1] To store information, memory devices make use of a physical property that displays hysteresis in response to an applied electric field. The stored information is retrieved by measuring the actual state of the hysteretic property. Many different physical phenomena can be used to obtain a memory effect. Today's computer memories, for example, are based on the hysteresis of charging and discharging capacitors. A downside of this technology is that the stored charge tends to leak away and needs to be restored at regular time intervals. Volatile memories such as this are unsuitable for many applications. RFID tags, for example, do not have a constantly available power source as they derive power from the radio signal that they receive,^[2] which means that they cannot always perform a memory refresh operation in case it would be necessary to

prevent loss of information. An organic memory technology that can potentially be used for RFID tags is the write-once read-many (WORM) type of memory.^[3,4] The operation mechanism of these devices is similar to that of a safety fuse. Information can be stored using the resistive switching above a certain voltage level and the actual state of the fuse can be read at a lower voltage. However, once the resistive switching has occurred there is no way to

return the device to its former state so this technology is not suitable for applications that need to be able to adjust the stored information, e.g., applications that require a book-keeping capability. To obtain a more universally applicable memory technology one therefore needs to combine nonvolatility and rewritability.

Many efforts are ongoing toward a nonvolatile and rewritable memory device that can enable a viable memory technology for a wide range of applications. Some of these efforts are focused on metal–organic semiconductor–metal junctions,^[5,6] charge trapping effects in field-effect transistors,^[7–9] and electromechanical switches,^[10] to name but a few.^[11] In this Review Article, we aim to capture the developments for one particular approach, i.e., those based on ferroelectricity. In this section we introduce ferroelectricity, explain why this physical mechanism has a great potential for enabling an organic memory technology and we take a look at the available organic ferroelectric materials. In Sections 2 to 4 we focus on three of the most important memory device concepts based on ferroelectricity, namely ferroelectric capacitors, field-effect transistors, and diodes. Section 5 looks at the construction of multi-bit memories by the integration of discrete memory elements. Finally, some challenges for future organic ferroelectric memories are highlighted in Section 6.

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1.1. Ferroelectricity

Ferroelectricity was discovered in 1921 in Rochelle salt ($\text{KNa}(\text{C}_4\text{H}_4\text{O}_6) \cdot 4\text{H}_2\text{O}$).^[12] It has been directly recognized that the polarization response of ferroelectrics can potentially be used for memory applications. However, applications for ferroelectric materials have been found in many other areas as well, as discussed recently by Scott.^[13] The term ferroelectricity itself was coined as such because of the analogy between the electrical properties of ferroelectrics and the magnetic properties of ferromagnets. The dielectric displacement D and polarization P

of ferroelectrics vary with the electric field E in the same general manner as the magnetic field B and magnetization M of ferromagnets vary with the magnetizing field H . Ferroelectrics show an electric hysteresis with loops distorted by an amount corresponding to a remanent polarization P_r .

For true ferroelectricity the remanent polarization has to originate from the alignment of intrinsic dipole moments inside a crystalline material.^[14] Mobile charges inside some permeable medium can achieve an electric hysteresis as well, but these charges are not in thermal equilibrium and will return to an equilibrium ground state with time when the applied field is removed. The correct identification of ferroelectricity requires close attention because of this.^[15] Only crystalline materials can give rise to ferroelectricity because intrinsic dipole moments in amorphous materials will have a random orientation, yielding a zero polarization overall. The crystal structure of ferroelectrics also needs to be such that the dipole moments do not cancel each other out completely. Consequently, the crystal symmetry should not be too high. Many ferroelectrics have a phase transition at elevated temperatures where the higher crystal symmetry negates the ferroelectricity.

Another rudimentary requirement for ferroelectricity is that polarization switching occurs below the dielectric breakdown field of the material. Ferroelectrics have a coercive field (E_c) which is often defined as the minimum field that is required to switch the full remanent polarization. Ferroelectric switching is an activated process that depends both on temperature and the applied field strength.^[16] The switching mechanism generally involves the nucleation and growth of ferroelectric domains in which all the dipole moments have the same orientation.

Ferroelectric polarization gives rise to a depolarization field, just like dielectric polarization.^[17] In the absence of an externally applied field, the depolarization field can negate any ferroelectric polarization. To stabilize the polarization one therefore needs to supply compensation charges at the surfaces of the material. For ferroelectric thin films this can be done by placing a conductive material on both surfaces and connecting the two (*i.e.*, short-circuit conditions). Any additional polarization can then be compensated for by charges that flow from one surface to the other.

The ferroelectric properties of a material are evident from charge displacement versus applied field measurements on thin-film capacitors, as illustrated in Figure 1. At low fields the applied field does not affect the ferroelectric polarization and the measurement shows only a linear dielectric displacement. At field strengths close to the coercive field the ferroelectric starts to polarize and at high fields it saturates because the maximum amount of polarization inside the material has been reached. Under saturated conditions the intersections with the x-axis and y-axis are usually identified as the coercive field and the remanent polarization of the material, respectively. Memory devices make use of the hysteresis by associating the polarization states $+P_r$ and $-P_r$ with a Boolean 1 and 0 that forms the basis for most logic circuits in use today.

If the charge compensation is arranged in an ideal way then the polarization states in a ferroelectric thin-film capacitor can in principle be sustained for an infinite amount of time because the electric fields in and outside the material are zero.^[17] This aspect of ferroelectricity is one of the main features that make it



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Paul W. M. Blom is since 2009 CTO at the Holst Centre, Eindhoven, The Netherlands and part-time professor at the University of Groningen where he is head of the group Physics of Organic Semiconductors. He received his Ph. D. Degree in 1992 from the Technical University Eindhoven. In 1992 he joined Philips Research Laboratories, where he was engaged in thin-film devices,

polymer light-emitting diodes, and rewritable optical storage research. In May 2000 he was appointed as a Professor of Physics at the University of Groningen, where he is working in the field of electrical and optical properties of organic semiconducting devices.



Dago de Leeuw is a research fellow at Philips Research Laboratories, Eindhoven, The Netherlands, and professor in molecular electronics at the University of Groningen, The Netherlands. His PhD degree was obtained at the Free University of Amsterdam in 1979. He has worked on materials science and technology of phosphors, high- T_c

superconductors, laser ablation, ferroelectrics, and polymer electronics. His current research interests are molecular electronics, nonvolatile data storage and biosensors.

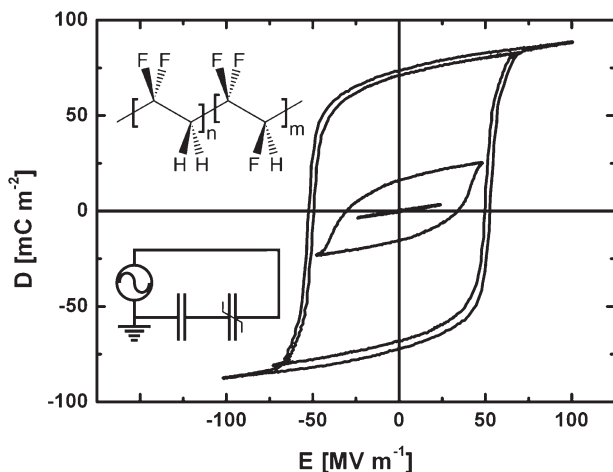


Figure 1. Charge displacement D vs applied field E measurement of a ferroelectric thin-film capacitor. The material used was poly(vinylidene fluoride-trifluoroethylene) with a layer thickness of $1.7\ \mu\text{m}$. The upper inset shows the chemical structure of this material. The lower inset presents the Sawyer–Tower circuit used for the measurement. Adapted from [18].

appealing for memory applications. In practice there can be interfacial defect layers between the ferroelectric and the compensation charges that can destabilize the polarization. This depolarization effect becomes stronger as the ferroelectric film thickness is reduced. The ferroelectricity can also be adversely affected by other things such as conductivity inside the ferroelectric or trapped charges at the interfacial defect layers. However, modern inorganic ferroelectric materials perform well enough for memory applications, as evidenced by their commercial availability.^[14] The retention time required by the industry is about 10 years.^[19]

1.2. Organic Ferroelectric Materials

Most of the activity surrounding organic ferroelectric materials is focused on PVDF [polyvinylidene fluoride; $(\text{CH}_2\text{CF}_2)_n$] and its copolymer P(VDF-TrFE) [poly(vinylidene fluoride-trifluoroethylene); $(\text{CH}_2\text{CF}_2)_n\text{-(CHFCF}_2)_m$]. The molecular structure of P(VDF-TrFE) is illustrated in Figure 1. A number of other organic ferroelectric materials are known to exist,^[20,21] but PVDF has several advantageous properties including a relatively large remanent polarization, a short switching time and a good thermal stability. By contrast, ferroelectric nylons for example show a switching time that is longer than that of PVDF by several orders of magnitude at the same applied field.^[20] The ferroelectricity of PVDF stems from the dipole moments in the molecule that can be aligned with the applied field by a rotation of the polymer chain, as illustrated in Figure 2. The dipole moments originate predominantly from the presence of the strongly electronegative fluorine atoms. For a detailed discussion about the ferroelectric properties of PVDF and their origins the reader is referred to a number of excellent review articles.^[22,23]

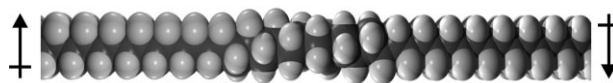


Figure 2. Artistic illustration of the dipole switching event in PVDF. On the left, the larger fluorine atoms are on top and the dipole moment points upwards. Toward the right, the molecule rotates around its axis, bringing the dipole moment along with it.

PVDF thin films processed from the melt or from a solution are not ferroelectric because the crystal structure and stereochemical conformation are such that the dipole moments cancel each other.^[23] To make these films ferroelectric one needs to perform additional steps such as stretching to force the polymer into another conformation. These additional steps can be avoided by using P(VDF-TrFE) instead of PVDF. Solution-processed films of P(VDF-TrFE) are ferroelectric straight away due to the steric hindrance from the additional fluorine atoms in polytrifluoroethylene (PTrFE) that induce an all *trans* stereochemical conformation that aligns the direction of the dipole moments. P(VDF-TrFE) thin films do require an annealing step at $140\ ^\circ\text{C}$ in order to raise the crystallinity of this semicrystalline polymer and concomitantly enhance its ferroelectric response.^[24] This annealing step does not eliminate any applications for PVDF because this temperature is compatible with a wide range of substrates and organic electronic materials.

The durability of P(VDF-TrFE) and its general usability for electronic device applications is evident from its widespread use for piezoelectric sensors and actuators.^[25] PVDF is produced on an industrial scale and sold with brand names such as Solef and Kynar. One of the main applications is as a protection coating due to its abrasion resistance, stiffness, nonflammability, radiation tolerance, and resistance to harsh chemicals.^[20] PVDF and P(VDF-TrFE) require no special precautions for handling and storage.

The potential for creating a nonvolatile memory technology based on P(VDF-TrFE) was already recognized over two decades ago but this has not yet led to any commercial memory products.^[26] In contrast, memory technologies that use inorganic ferroelectric materials have been available commercially for over a decade.^[14] However, the situation could well change in just a few years because several business media reports and patent applications indicate that a memory technology based on ferroelectric polymer capacitors is at an advanced stage of development.^[27,28] This affirms that there is a large potential for organic nonvolatile memory technologies based on ferroelectricity.

2. Ferroelectric Capacitors

One of the simplest types of ferroelectric memory devices is the thin-film capacitor. Information is stored by aligning the direction of the internal polarization either up or down with an applied field. To retrieve the information one applies a switching voltage to obtain a high or a low charge displacement current response depending on whether the internal polarization was aligned or not with the direction of the applied field. Ferroelectric capacitors

therefore have a so-called destructive read-out since a read operation can affect the stored information. If the polarization direction was changed during the read operation then a reset voltage needs to be applied afterwards.

Here, we will start with a brief look at the history of attempts to attain low-voltage switching in P(VDF-TrFE). Due to the relatively high coercive field of 50 MV m^{-1} of P(VDF-TrFE) sub-100 nm thick layers are required in order to arrive at a switching voltage below 10 V. Two seminal papers from 1986 and 1995 established the fact that spin-coated films with a sub-100 nm thickness have an extremely retarded ferroelectric response as compared to the bulk material,^[29,30] which implied that P(VDF-TrFE) is unsuitable for low-voltage memory applications. In 1998 a report about thin films made with a Langmuir–Blodgett deposition technique appeared that showed that a ferroelectric response can be retained down to layer thicknesses of 15 nm.^[31] Unfortunately, these films are probably even less suitable for applications than the aforementioned spin-coated films because the switching times are longer by orders of magnitude.^[32,33] Two reports in 2001 and 2002 claimed some improvement for spin-coated films by optimizing the annealing conditions,^[34,35] but the improvements were relatively minor and so the prospects for memory applications of P(VDF-TrFE) remained bleak.

The situation came to a turnaround due to a serendipitous discovery that was published in 2004.^[36] Figure 3 shows charge displacement measurements that established that the ferroelectric response remains almost the same when the layer thickness is reduced from 210 to 65 nm. These measurements demonstrated that it is possible to have sub-10 V switching while retaining the remanent polarization and switching times of the bulk material. The low-voltage switching behavior was obtained by using a bottom electrode stack that includes an interfacial layer of the conductive polymer PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)]. The top electrode consisted of vapor-deposited gold. At the time when we were attaining the results above with PEDOT:PSS others filed a patent application on a similar idea.^[37] The existence of this

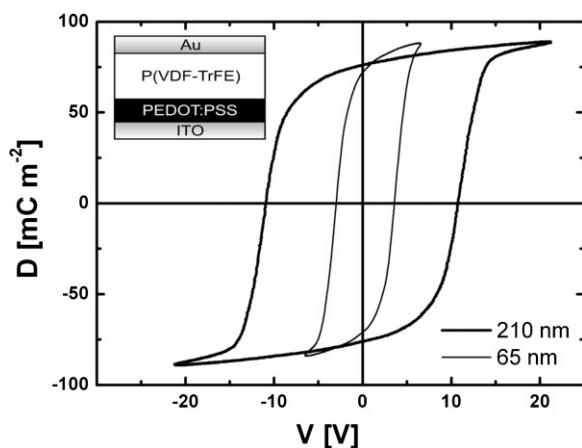


Figure 3. Displacement charge D versus applied voltage V hysteresis loop measurements on capacitors with a ferroelectric layer thickness of 210 and 65 nm. The capacitors have a PEDOT:PSS bottom interface, as shown in the inset. Adapted from [36].

application suggests also that conductive polymers can enable memory applications based on the use of P(VDF-TrFE).

Xu et al. later published a report about capacitors with the conductive polymer Ppy:PSS [polypyrrole-poly(styrene sulfonic acid)] as a bottom and top interface.^[38] Ferroelectric capacitors with a layer thickness of 50 nm were shown to have the same ferroelectric properties as the bulk material. The switching cycle endurance properties of the capacitors were also investigated. When a ferroelectric undergoes a large number of switching cycles then so-called fatigue can occur, which manifests itself in a lowering of the remanent polarization, higher coercive fields and longer switching times. Cycle endurance is very important because ferroelectric capacitors receive a large number of read and write cycles during a normal product lifetime, due to the destructive read-out operation mechanism of ferroelectric capacitors. As presented in Figure 4, the polarization degradation is limited to a value of 15% after 10^7 cycles at an elevated temperature of 60°C .

The reason why the observed low-voltage switching behavior as obtained by inserting conductive polymers was not obtained before lies in the fact that all previous investigations used aluminum top and bottom electrodes.^[29–32,34,35] X-ray photoelectron spectroscopy (XPS) measurements have indicated that aluminum reacts with P(VDF-TrFE) regardless of whether the aluminum was deposited onto P(VDF-TrFE) or the other way around.^[39] The chemical reaction between aluminum and P(VDF-TrFE) leads to the formation of nonferroelectric or “dead” layers near the electrode interfaces, the presence of which can be derived from the retarded switching kinetics that are induced.^[40,41] One can also avoid the reaction by using the chemically more inert element gold and, as expected, this yields an improvement of the ferroelectric response of P(VDF-TrFE) thin-film capacitors as well.^[42,43]

3. Ferroelectric Field-Effect Transistors

A disadvantage of using ferroelectric capacitors for memory applications is that the charge displacement response scales with

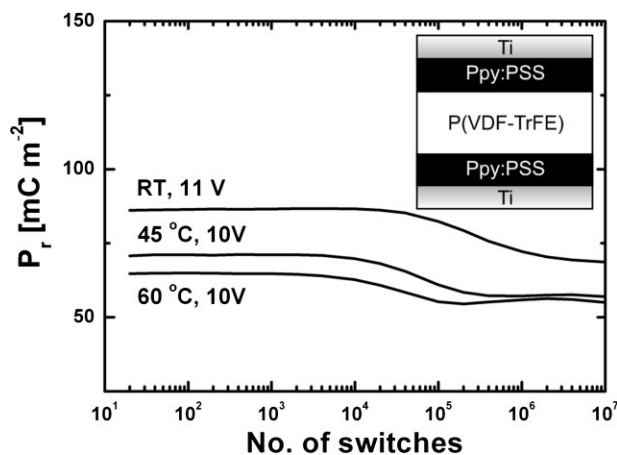


Figure 4. Remanent polarization P_r versus number of switching cycles for ferroelectric capacitors with a P(VDF-TrFE) layer thickness of 50 nm, measured at room temperature (RT), 45 and 60°C . The inset illustrates the device structure with a Ppy:PSS top and bottom interface. Reprinted with permission from [38]. Copyright 2007, American Institute of Physics.

the surface area of the capacitors. Downscaling of the lateral dimensions lowers the displacement currents and at some point they can no longer be detected reliably. This downscaling issue will be discussed in more detail in Section 5.1. Ferroelectric field-effect transistors (FeFETs) and ferroelectric diodes alleviate this scaling problem because the resistive switching that they provide results in a high or a low current response that can be sampled for an arbitrary amount of time. In a FeFET a ferroelectric insulator is used as a gate dielectric. The ferroelectric polarization gives rise to a memory functionality due to the attenuation of the charge carrier density in the semiconductor channel. A gate voltage can align the ferroelectric polarization and induce either a high or a low semiconductor channel conductance that remains after removing the gate voltage. The conductance can be sampled at any time with a low drain voltage that does not disturb the ferroelectric polarization. In this way, FeFETs provide a nonvolatile memory combined with a nondestructive read-out functionality.

FeFETs based on inorganic materials have had problems with charge trapping at the ferroelectric-semiconductor interface and thermal stability issues,^[14,44,45] which are the main reasons why inorganic FeFETs have not yet been implemented in commercial products. Fortunately, organic FeFETs do not suffer extensively from these particular interface problems mainly due to the fact that the interactions inside the organic materials are relatively weak, i.e., the materials are held together by Van der Waals and/or hydrogen bonding rather than stronger Coulombic interactions. However, organic FeFETs do pose challenges in other ways. Here, we will review the results obtained with organic FeFETs based on polymer and small molecule semiconductors and discuss the origins of their memory functionality.

3.1. Polymer Semiconductors

A report in 2005 demonstrated the first FeFET based on a polymer semiconductor and it used the amorphous polymer MEH-PPV [poly(2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylenevinylene)].^[18] The transfer measurement presented in Figure 5 demonstrates the basic functionality that was achieved. At an increasingly negative gate bias, the drain current shows an off-to-on transition at the coercive voltage of the gate dielectric. The drain current remains high when the gate bias returns to zero due to the hole accumulation that is induced by the polarization of the gate dielectric. At a positive gate bias close to the coercive field the current returns to an off-state. Depending on the history of the applied gate voltage, the drain current can change by a factor of 10^4 at zero gate bias. A control experiment was performed to confirm that the bistability is due to ferroelectricity and not due to some unintended artifact. For this experiment, transistors were prepared where the P(VDF-TrFE) was replaced by PTrFE. PTrFE is semicrystalline and highly polar just like P(VDF-TrFE) but its ferroelectricity is negligible.^[22] In this way, the ferroelectricity is turned off while everything else is kept the same as much as possible. A negligible hysteresis was obtained with these transistors, confirming that the observed bistability in the P(VDF-TrFE) FeFETs originated from the ferroelectricity of the gate dielectric.

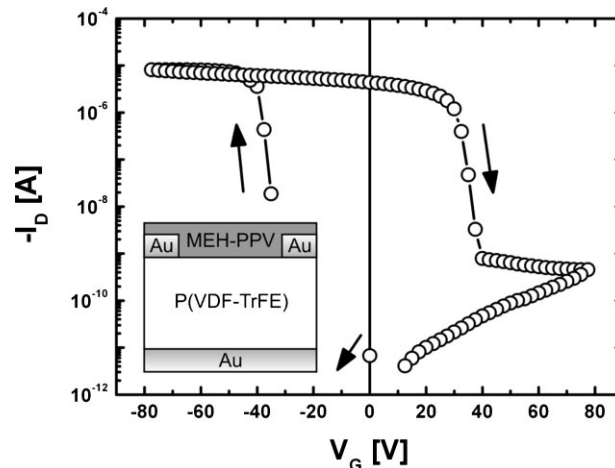


Figure 5. Transfer measurement on a polymer FeFET with a gate dielectric thickness of $0.85 \mu\text{m}$. The inset illustrates the device structure with MEH-PPV as the semiconductor. Adapted from [18].

The FeFETs were subjected to a range of tests to quantify their memory performance further. The switching time was less than 1 ms. Memory retention tests under storage conditions showed that the drain current on/off ratio did not change during a period of one week. Programming cycle endurance measurements showed that the devices still functioned well after 1000 cycles.

The reported FeFETs had rather thick gate dielectric layers and, consequently, high switching voltages. Soon after this report however, FeFETs were demonstrated that can operate at 15 V.^[46] The feasibility of low voltage switching is evident from the results with ferroelectric capacitors described in Section 2, but making field-effect transistors with thin gate dielectrics poses additional challenges. The processing conditions of P(VDF-TrFE) thin films were optimized to obtain high quality films that are suitable as a gate dielectric. The MEH-PPV semiconductor was replaced by rr-P3HT [regioregular poly(3-hexylthiophene)] because this polymer has a higher field-effect mobility which enables the use of lower drain voltages to measure the channel conductance. The drain voltage lowering was necessary because the voltage could otherwise affect the polarization state of these thin ferroelectric films. The achieved mobility was $8 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ which was a significant improvement over MEH-PPV.

The mobility value obtained in rr-P3HT was still inferior to previously reported values of up to $0.1 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[47] The relatively low mobility was caused by the high surface roughness of P(VDF-TrFE) films which can adversely affect the ferroelectric-semiconductor interface.^[48] The adverse effect on the mobility was elegantly solved by reversing the layer stack, i.e., by depositing P(VDF-TrFE) onto rr-P3HT instead of the other way around.^[49] By placing the rr-P3HT underneath, the interface smoothness is not determined by the top surface of P(VDF-TrFE) but by that of rr-P3HT and this surface is inherently smoother than a P(VDF-TrFE) surface. Furthermore, by optimizing the rr-P3HT thin film processing a surface roughness of just 0.7 nm (rms) was achieved, as measured by AFM. With this smooth ferroelectric-semiconductor interface a high field-effect mobility

of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved. This result facilitates a further reduction of the drain voltage used to sample the channel conductance during a read operation.

3.2. Small Molecule Semiconductors

Almost all reports about organic FeFETs based on small molecule semiconductors have used pentacene. As noted by several authors,^[50–52] combining pentacene with P(VDF-TrFE) is problematic due to the high surface roughness of P(VDF-TrFE) thin films. For a high field-effect mobility in pentacene transistors one needs to obtain a high degree of crystallinity. The high crystallinity can be obtained by optimizing the crystal growth process but this works best on flat surfaces.^[48] It is deemed impossible to avoid this interface roughness problem by reversing the layer order, i.e., by depositing the P(VDF-TrFE) on top of the pentacene. The organic solvents that would be required for the deposition of P(VDF-TrFE) onto pentacene are known to be detrimental to the pentacene surface.^[53] As a result, the reported mobilities are relatively low. The highest mobility attained thus far in pentacene FeFETs is $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[54] To achieve this mobility value Nguyen et al. stretched their P(VDF-TrFE) thin films to simultaneously enhance the crystallinity and lower the surface roughness. The transfer measurements had a similar shape as in Figure 5 and the drain current on/off ratio was 10^4 .

A few reports describe a combination of materials that do not appear to have a ferroelectric-semiconductor interface roughness problem. Matsuo et al. used pentacene on top of TGS [triglycine sulphate] ferroelectric crystals and Schroeder et al. used pentacene on top of an amorphous nylon material.^[55–58] Significant drain current modulation ratios were obtained and in the case of TGS also low voltage operation was demonstrated. However, both devices also had some shortcomings. The FeFETs based on TGS had a low on/off ratio after a data retention test. Nylons have the disadvantage that their switching times exceed seconds, which is four orders of magnitude slower than P(VDF-TrFE).^[20] With intrinsic problems such as the ones above, it is difficult to foresee any memory applications using these materials.

The use of vinylidene fluoride oligomers are an intriguing approach toward combining small molecule semiconductors and organic ferroelectrics. The ferroelectric properties of these oligomers are better than those of the polymer in some respects and,^[59,60] unlike the polymer, they can be deposited by evaporation. This could facilitate a combination of oligomers with small molecule semiconductors because either material could be vapor deposited onto the other. This way of combining the ferroelectric and the semiconductor could potentially enable a smooth interface.

3.3. Origin of the Bistability in Organic Ferroelectric Field-Effect Transistors

A fundamental constraint for the operation of FeFETs is that the potential induced by band-bending in the semiconductor (V_{bb})

should not exceed a value that causes a depolarization of the ferroelectric layer.^[61] Under short-circuit conditions the depolarization field in the ferroelectric equals V_{bb} divided by the ferroelectric layer thickness. The possibility therefore exists that, as the ferroelectric layer thickness is reduced to obtain low-voltage operation, the ferroelectricity becomes unstable. For polymer FeFETs based on MEH-PPV the V_{bb} was derived from a measurement of the surface charge density that is permanently induced by the ferroelectric.^[18] V_{bb} turned out to have a low value of 0.5 V. This shows that the band bending will not stop the development of FeFETs that operate at low voltages.

Another important question with regards to the operation of organic FeFETs is what happens in the off-state of the device. In Figure 5 it is not clear what happens to the polarization state of the ferroelectric after depleting the semiconductor: the ferroelectric either switches into the reverse polarization keeping the semiconductor depleted, or the ferroelectric may depolarize due to the lack of free electrons in the p-type semiconductor that compensate the ferroelectric polarization charge. To address such questions, experiments were performed with ferroelectric metal-insulator-semiconductor (MIS) diodes.^[62] Figure 6 presents a capacitance versus gate voltage measurement on a ferroelectric MIS diode. The $C-V$ curve has a marked nonlinearity and hysteresis at negative biases. This behavior was also observed in P(VDF-TrFE)-only capacitors and stems from the bias-field dependent permittivity of P(VDF-TrFE).^[63] At a positive bias equal to the coercive field the semiconductor goes into depletion which results in a drop in capacitance. On return to zero gate bias the capacitance increases again. This increase demonstrates that the ferroelectric is not keeping the semiconductor depleted. It can therefore be concluded that the ferroelectric depolarizes when the MIS diode is forced into depletion due to the lack of compensation charges provided by the semiconductor. The observed depolarization behavior indicates that organic FeFETs

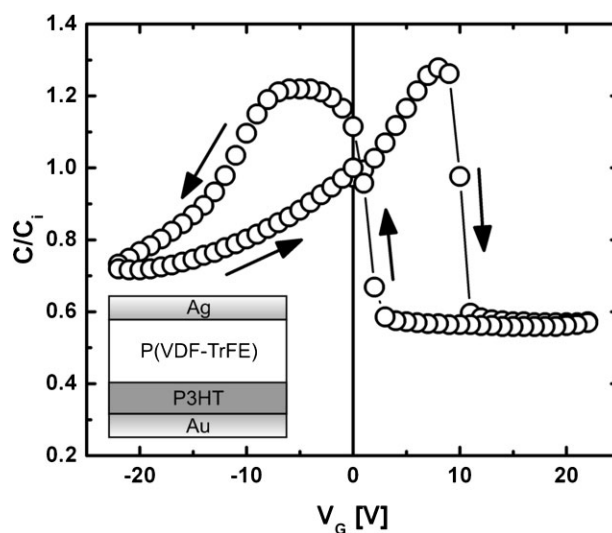


Figure 6. Capacitance C versus gate voltage V_G measurement on a ferroelectric MIS diode with a P(VDF-TrFE) gate dielectric film thickness of 220 nm. The capacitance C was divided by the insulator capacitance C_i . The inset illustrates the device structure with P3HT as the semiconductor. Adapted from [62].

work differently than inorganic FeFETs. Inorganic FeFETs can switch between accumulation and inversion to provide compensation charges to the ferroelectric in both states.

The discussion above regarding the on- and off-state in organic FeFETs broadly explains the persistence of the on- and off-state. In the on-state the ferroelectric is polarized and in a thermodynamically favorable state and therefore stable. In the off-state the ferroelectric is not in equilibrium because it is depolarized. The retention of the off-state remains long because under short-circuit conditions the appearance of a spontaneous polarization takes a long time.

In order to avoid a depolarized state in organic FeFETs the semiconductor needs to supply compensation charges for both ferroelectric states. It has been demonstrated that n-type FeFETs can be achieved with the methanofullerene PCBM [(6,6)-phenyl-C₆₁-butyric acid methyl ester].^[64] Moreover, both n- and p-type behavior can be obtained in a single FeFET with the use of an ambipolar organic semiconductor comprising a blend of MEH-PPV and PCBM.^[65] The transfer measurement of an ambipolar FeFET that is presented in Figure 7 is essentially the same as for the unipolar FeFET based on MEH-PPV in Figure 5, except that the hole accumulation is mirrored on the right side of the figure due to an electron accumulation. Evidently, this FeFET can switch between hole and electron accumulation. An obvious disadvantage in this case is that the drain current at zero gate bias is no longer bistable because the hole and electron current response is about the same. One could address this issue by using a novel way of probing the state of the ferroelectric polarization, such as measuring the sign of the field-effect mobility using a small applied gate voltage. However, it may be simpler to tune the blending ratio of the semiconductor to re-obtain a certain degree of bistability. Further developments on these ambipolar devices were limited because they suffer from interface issues caused by the high surface roughness of P(VDF-TrFE). The roughness problem has already been solved for p-type FeFETs by reversing the layer stack, as described in Section 3.1. This solution could possibly work for ambipolar FeFETs too.

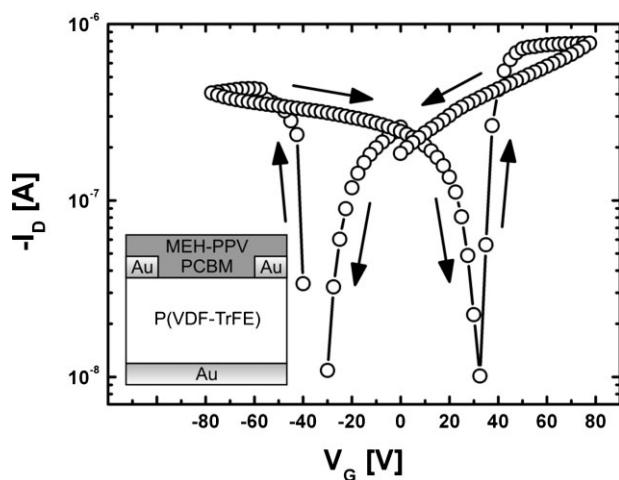


Figure 7. Transfer measurement on an ambipolar polymer FeFET with an insulator layer thickness of 0.9 μm . The inset illustrates the device structure with a blend of MEH-PPV and PCBM as the semiconductor. Adapted from [65].

Another approach to obtain both n- and p-type behavior in a single FeFET has recently been demonstrated by Zheng et al.^[66] They prepared a graphene-based FeFET with a P(VDF-TrFE) gate dielectric and demonstrated that the FeFETs have n- and p-type accumulation behavior. The authors also obtained a modest bistability in the FeFETs of up to 3.5 at zero gate voltage. However, the bistability had to be obtained by using asymmetric voltage sweeps that induce either a complete or an incomplete polarization inside the P(VDF-TrFE) because the n- and p-type responses of graphene transistors are equivalent. The memory operation did not rely on the direction of the ferroelectric polarization. The state with incomplete polarization may prove to be relatively unstable in time as the ferroelectric is not in thermodynamic equilibrium. A great advantage of using graphene is the high field-effect mobility of up to $200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. The authors argue that the mobility should enable a read-out operation that is shorter than 10 fs.

4. Ferroelectric Diodes

FeFETs have a rather elaborate device structure which will complicate the construction of a larger integrated memory technology. The relatively simple device structure of a ferroelectric capacitor is more advantageous in this respect. However, as noted above, ferroelectric capacitors have a limited scaling capability caused by the finite charge displacement that they produce. Ferroelectric diodes can alleviate this scaling problem because they provide resistive switching. In this way, ferroelectric diodes combine the advantages of ferroelectric capacitors and FeFETs. For this reason there is an ongoing research activity to realize resistive switching in inorganic ferroelectrics integrated in a diode structure.^[67] Inorganic ferroelectrics are wide-band-gap semiconductors, but the presence of lattice defects such as vacancies can give rise to a finite electrical conduction.^[16] A bistable conduction has been demonstrated in a ferroelectric Schottky diode based on lead titanate (PbTiO_3) more than a decade ago.^[68] The bistability stems from a modulation of the depletion width by the ferroelectric polarization. For a polarization parallel to the built-in field the depletion width is small and the resistance of the diode is low. For a polarization anti-parallel to the built-in field, the depletion width is large and the resistance is high. The resistance states can be probed at a low bias that does not affect the ferroelectric polarization. A major problem for these devices is that ferroelectricity and electrical conductivity are two orthogonal physical properties, i.e., it is difficult for them to co-exist in a single compound. Doping the material is necessary because the depletion width needs to be adjusted. However, the additional free charge carriers can neutralize the polarization charges, with a deteriorated ferroelectric response as a result. Evidently, the challenge is to develop a storage medium that enables an independent tuning of the conductive and ferroelectric properties.

The fact that polymer materials can be solution-processed creates a new possibility to arrive at ferroelectric diodes. Polymer blends tend to phase separate due to their low enthalpy of mixing and small entropic gain.^[69] One can therefore blend an insulating ferroelectric and a semiconducting polymer to obtain a composite with distinct ferroelectric and semiconducting areas. This

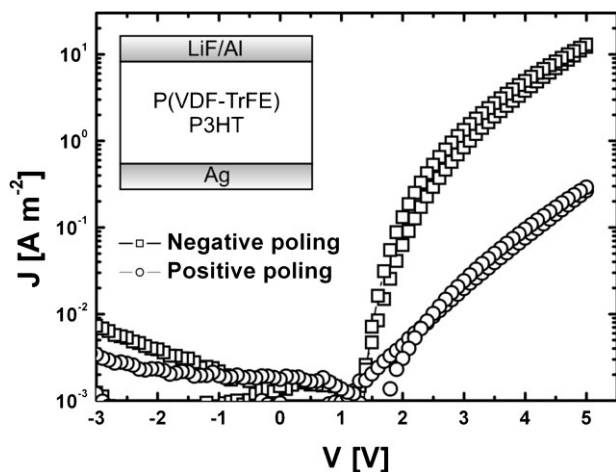


Figure 8. Current density J versus applied voltage V for a ferroelectric diode with a phase separated blend layer comprising 90% P(VDF-TrFE) and 10% P3HT and a layer thickness of 230 ± 20 nm after negative and positive poling with respect to the bottom electrode. The inset illustrates the device structure. Adapted from [70].

approach allows for an independent tuning of the conductive and ferroelectric properties of the composite film through the choice of polymers and blending ratios.

A nonvolatile resistive memory was recently demonstrated using phase-separated films of P(VDF-TrFE) and the polymer semiconductor rir-P3HT [region-irregular poly(3-hexylthiophene)].^[70] Current–voltage measurements on a rectifying diode with a LiF/Al top contact and a silver bottom contact are presented in Figure 8. Application of a voltage higher than the coercive field of the ferroelectric with a negative or positive polarity produces either a high or a low current response. The observed switching was attributed to changes in the charge injection at the silver/rir-P3HT contact. The proposed mechanism is illustrated in Figure 9. The injection barrier at the silver/rir-P3HT contact is 0.6–0.7 eV,^[71] which leads to an injection limited charge transport in the rir-P3HT phase. As the ferroelectric polarizes in response to an applied

voltage, the polarization charges are compensated by the metal electrode and the semiconductor. The presence of compensated charges accumulated in the rir-P3HT phase results in band bending that lowers the injection barrier. The current response becomes space-charge limited instead of injection limited.^[72] The top contact in this case is a LiF/Al hole blocking contact. For the top contact the ferroelectric polarization is not sufficient to lower the injection barrier and it therefore remains blocking. The final result is a rectifying diode where the current can be modulated by aligning the ferroelectric polarization.

Retention, switching time and cycle endurance measurements on the blend devices gave a response, i.e., comparable to those of the state-of-the-art polymer FeFETs.^[18] The retention time of the devices was demonstrated to be close to 10^6 s within the experimental time interval. The long retention time stems from the intrinsic nonvolatile nature of ferroelectricity. The switching time of the blend is the same as that of pristine P(VDF-TrFE). As with P(VDF-TrFE) capacitors, low voltage switching in these devices should be attainable by reducing the film thickness.

Some details of the operation mechanism of polymer ferroelectric diodes are still not clear. The remanent polarization of the films cannot be measured directly using charge displacement measurements due to the high leakage current through the rir-P3HT phase.^[72] As an alternative, the ferroelectric properties of these films were demonstrated by capacitance–voltage (C – V) measurements. P(VDF-TrFE) capacitors exhibit a distinct butterfly-shaped C – V curve that is caused by the switching of dipoles.^[63] It was demonstrated that the blended films have a similar C – V hysteresis as for the pristine films.

5. Integrated Memories

To achieve a memory technology one needs more than a single device that works. Multiple devices need to be integrated into a larger array of memory bits for nearly every foreseeable application. Doing so brings along some unique challenges such as the capability of addressing an individual bit in this larger array both for reading and writing information. Here, we take a look at integration issues for each of the three types of devices that were discussed above.

5.1. Ferroelectric Capacitors

The simplest multi-bit structure that one can make with ferroelectric capacitors has a crossbar geometry, i.e., the unpatterned ferroelectric layer is sandwiched between rows and columns of metal electrode lines where each intersection makes up one capacitor. Current memory technologies based on inorganic ferroelectric materials do not have this structure; however, because of the so-called half-select problem.^[14] To illustrate this problem let us suppose that we want to address one bit in

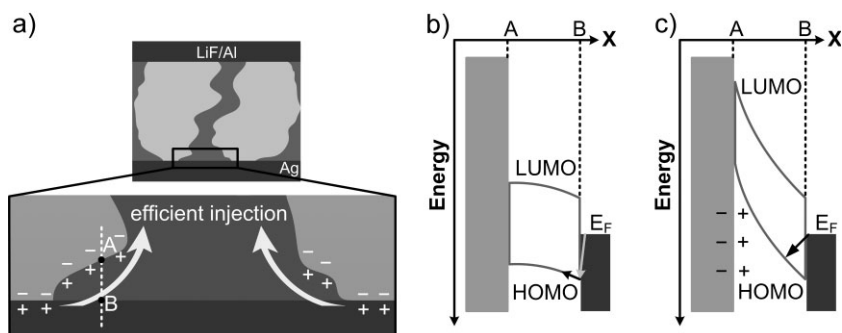


Figure 9. Schematic presentation of the operating mechanism of a polymeric ferroelectric interpenetrating network. a) Schematic cross-section of a diode based on a network of semiconducting and ferroelectric polymers. b) Band diagram at the bottom silver contact of an unpoled diode along the cross-section A–B. c) Band diagram at the bottom silver contact of a poled diode along the cross-section A–B. Poling of the ferroelectric material yields opposite charges at the ferroelectric–semiconductor interface, induces band bending in the semiconductor and leads to enhanced charge injection.

the array. To achieve this we can, for example, apply half the switching voltage ($+1/2V_s$) on one row and another half with opposite polarity ($-1/2V_s$) on one column whilst keeping all other electrodes grounded. Only the selected bit would be addressed with this procedure if ferroelectrics had a true threshold voltage for switching, but this is unfortunately not the case.^[73] The repetitive application of $\pm 1/2V_s$ can in fact alter the polarization state of neighboring capacitors which leads to data corruption. Current inorganic ferroelectric memories therefore use an active matrix that integrates a selection transistor for every memory element, at the cost of more fabrication steps and an increased surface area per bit. However, according to several patent applications it is feasible with P(VDF-TrFE) to use a passive matrix, i.e., a crossbar memory structure.^[74,75] It is claimed that the relatively long switching time of P(VDF-TrFE) compared to those of inorganic ferroelectrics enables the application of a complicated voltage pulse procedure within a certain time-frame that reduces or avoids the half-select problem. If a passive matrix can indeed be used then this is highly advantageous because of the lower production costs and the reduced surface area per bit.

Another patent disclosure claims that the relatively long switching time of P(VDF-TrFE) lessens the problem of destructive read-out.^[76] Information is most commonly derived from ferroelectric capacitors by applying a switching voltage and measuring the charge displacement response, which will be either high or low, depending on the initial state of the ferroelectric polarization. This destructive read-out leads to adverse effects such as fatigue and a relatively high power dissipation caused by the high number of read and write operation cycles. However, according to the patent, the relatively long switching time of P(VDF-TrFE) makes it easier to intervene during the switching event. It becomes possible to limit the duration of the switching voltage so that it is just long enough to read the stored information and short enough to leave most of the original ferroelectric polarization intact. One can then read the same device for a number of times before reaching a state where the polarization has decreased to such an extent that the polarization needs to be restored. This scheme has the additional advantage that it shortens the time it takes to retrieve information.

From the above it would appear that advanced voltage application procedures can enable the use of a passive matrix and a nondestructive read-out. An important issue that remains is area scaling. The surface area of the P(VDF-TrFE) capacitors can in principle be brought down to 100 nm^2 or less as evidenced by several experimental studies where small areas of a thin film are polarized with the aid of a conductive AFM.^[77,78] It has also been shown that it is possible to emboss P(VDF-TrFE) thin films into individual nanostructures with a large ferroelectric response.^[79] In practice however the surface area per bit may have a substantially larger minimum size. The charge displacement current that a ferroelectric capacitor produces decreases with area which can lead to an inability of sensing the current response. This issue is especially important in the case of integrated circuits because it can be difficult to avoid the creation of parasitic capacitances. The charge displacement response from these parasitics can vary depending on the position in the integrated circuit and in this way obfuscate the ferroelectric charge displacement.

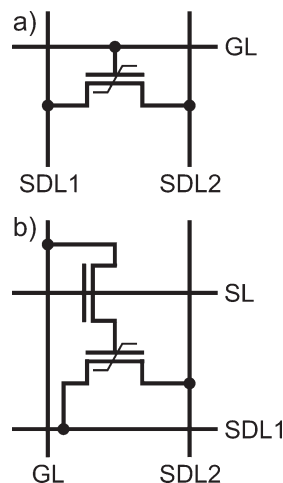


Figure 10. Schematic illustrations of single memory circuit elements based on FeFETs that reside in a larger array. a) A circuit element with one FeFET per cell, a gate line GL and two source-drain lines SDL1 and SDL2. b) A circuit element with one selection transistor and one FeFET per cell and an additional selection line SL.

5.2. Ferroelectric Field-Effect Transistors

The highest surface density for a memory circuit based on FeFETs can be obtained with the layout that is illustrated in Figure 10a. To store information a switching voltage is applied to the gate line GL. To retrieve the stored information one applies a read voltage between the two source-drain lines SDL1 and SDL2. However, this scheme has several drawbacks.^[80,81] The write operation suffers from the same half-select problem as the ferroelectric capacitor arrays in Section 5.1. Furthermore, the read operation actually requires the application of a gate voltage to all the nonaddressed cells along the SDL line of the addressed cell in order to turn these off, which can potentially disturb the polarization in these cells. Based on these considerations it seems likely that an active matrix circuit will be required, as illustrated in Figure 10b.^[82] To write one applies a voltage to the select line SL to turn the selection transistor on. Bits are then written by applying the appropriate switching voltage to the gate line GL. To read one applies a low voltage difference between SDL1 and SDL2 while SL and GL are kept grounded. This scheme should not disturb any of the nonaddressed cells during the read and write operations and allow for nondestructive read-out with a low voltage. It is perhaps possible to use the same ferroelectric insulator layer for the FeFETs as well as the selection transistors to reduce the number of processing steps because (unipolar) FeFETs fulfill the electrical requirements for a selection transistor. However, even if this turns out to be true, the number of required manufacturing steps for FeFETs will still be larger than for the simple ferroelectric capacitor passive matrix that was discussed in Section 5.1. The minimum surface area per bit may also turn out to be larger. Evidently, the nondestructive read-out functionality of FeFETs does come at a cost.

Sekitani et al. recently demonstrated the first integrated organic FeFET memory circuit based on P(VDF-TrFE).^[83] The circuits were fabricated with low-cost printing techniques and thermal evaporation. Their implementation combines two regular organic FETs with each FeFET to enable access to

individual bits. By connecting a 72-bit random-access memory circuit to a custom wireless communication circuit, the information contained in the circuit could be transmitted using radiowaves. These achievements could prove to be a step toward the development of low-cost reprogrammable RFID tags.

5.3. Ferroelectric Diodes

The most important advantage of ferroelectric diodes over FeFETs is that they can be integrated in a memory bit array with a simple crossbar geometry to obtain a high memory bit density. However, technologies that use both resistive switching and a crossbar geometry suffer from the so-called cross-talk problem. To illustrate this problem, let us suppose that we want to read the state of the device in the upper-left corner of Figure 11a, which is in its off-state and therefore has a high resistance. The other three neighboring devices are in the on-state, as represented by the absence of a resistor. If a voltage difference is applied to word line WL1 and bit line BL1 in order to read the resistivity of the upper-left cell the neighboring cells provide a leakage path. Consequently, the current will predominantly go along this path, which makes it impossible to read the logic state of the upper-left device. For larger memory circuits the measured resistance equals that of the selected cell in parallel with the resistances of the memory cells in all other word and bit lines. A reliable determination of the logic value therefore requires an electrical isolation of the cells. The solution to this problem is the addition of a rectifying diode in series with each resistive switching element, as illustrated in Figure 11b. In Figure 11b, the leakage path is disabled by the diode in the bottom-right corner because its direction opposes the current flow. By selecting appropriate biases on rows and columns each individual memory element can now be addressed. The possible size of the memory array is about equal to the rectification ratio squared.

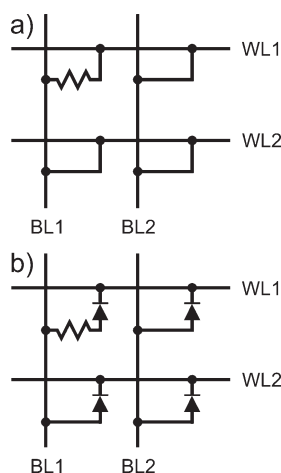


Figure 11. Schematic illustration of the cross-talk problem in crossbar arrays of devices with resistive switching. The cross-bars consist of the horizontal word lines (WL) and the vertical bit lines (BL). a) The four devices at each intersection have resistive switching alone. The upper-left is off, as represented by the resistor, and the other bits are on, as represented by the absence of a resistor. b) The same array as in (a) with integrated rectifying diodes.

In devices based on ferroelectric/semiconductor blends the cross-talk problem was addressed by fabricating a silver/rir-P3HT contact where the conductance is modulated between injection limited current and space charge limited current upon ferroelectric polarization. As shown in Figure 8 the diodes are both bistable and rectifying. The integration of these diodes into a memory array has not yet been demonstrated but further work is in progress. Another issue that needs to be addressed is that the crossbar approach presented here will face the same half-select problem as with the ferroelectric capacitors in Section 5.1. We emphasize however that several patent disclosures suggest that the half-select problem is alleviated with P(VDF-TrFE), as already mentioned in Section 5.1. The minimum surface area of the blended film diodes will be intrinsically limited by the extent of phase separation between the ferroelectric and the semiconductor. The length scale of the separation is currently around 200 ± 50 nm in the case of a blend with 10% P3HT. The emphasis of current work is on down-scaling the blend separation length scale.

6. Summary and Outlook

In the last five years there have been many significant developments towards the realization of organic memory devices based on ferroelectricity. The work horse is the ferroelectric copolymer P(VDF-TrFE). Table 1 presents the main features of the three most important memory technologies that have emerged. For comparison purposes the table also includes information on memory devices based on metal–organic semiconductor–metal junctions, as derived from a recent review by Yang.^[5] Out of these four technologies ferroelectric capacitors appear to be closest to entering the market, judging by several business media reports.^[27] To a large extent this success has been enabled by the low voltage switching that was demonstrated in capacitors with added interface layers of conducting polymers. It is in principle now possible to use low-cost solution-based processing techniques to make integrated memory circuits that consist of crossbar arrays of ferroelectric capacitors, e.g., by ink-jet printing metal contacts, conductive polymer interface layers and P(VDF-TrFE) thin films. As discussed in Section 5.1, some of the inherent problems of ferroelectric capacitor circuits appear to be surmountable, e.g., how to avoid data corruption in neighboring capacitors in an integrated memory circuit. However, the problem of limited surface area scaling of capacitors will always remain. A single P(VDF-TrFE) capacitor can scale to lateral dimensions of less than 100 nm^2 but in integrated memory circuits the scaling leads to a loss of signal, due to the finite charge displacement that the capacitors produce. The surface area limitation could lead to the emergence of memory technologies based on one of the other presented device concepts, i.e., the ferroelectric field-effect transistor and the ferroelectric diode based on ferroelectric/semiconductor phase-separated blends.

Polymer FeFETs facilitate simple, nondestructive read-out functionality whilst retaining the long retention time, short switching time and low-voltage operation of ferroelectric capacitors. As mentioned in Table 1, it has not yet been tested what the minimum lateral dimensions are for an organic FeFET. The lateral dimensions of the semiconductor channel should in

Table 1. An overview of the main features of several organic memory technologies. The information on metal–organic semiconductor–metal junctions was derived from a recent review by Yang [5].

	Ferroelectric capacitors	Ferroelectric field-effect transistors	Ferroelectric diodes [70]	Metal–organic semiconductor–metal junctions [5]
Resistive switching	No	Yes	Yes	Yes
Development stage	Near to market [27]	Basic research	Basic research	Basic research
Scalability for single cell	High [79]	Not tested yet—Limited by short channel effects	Not tested yet—limited by phase separation	Not tested yet—limited by filament formation [85]
Simplest devised cell in an array	1C	2T	1D	1D1R or 1T1R
Integration	Limited by signal loss [14]	Two or more devices per bit [83]	Not tested yet—crossbar array deemed possible	Not tested yet—crossbar array deemed possible
Fast read-out (< 1 μs)	No	Yes	Yes	Yes
Fast writing (< 1 ms)	Yes	Yes	Yes	Yes
Low switching power	Yes	Yes	Yes	Yes
Cycle endurance	>10 ⁷ [38]	>10 ³ [18]	>10 ³	>10 ⁶
Nonvolatility	Yes	Yes	Yes	Yes
Retention time	Probably infinite [16]	>3 × 10 ⁶ [84]	>5 × 10 ⁵	>5 × 10 ⁴
Patterning the storage medium	No	No	No	No

principle have the same scalability as a ferroelectric capacitor, i.e., less than 100 nm². However, the minimum channel size will most likely be limited by short channel effects, which are known to occur at significantly larger lateral dimensions.^[86] The information density of integrated memory circuits based on FeFETs will also be limited by the need for additional transistors that facilitate access to individual FeFETs. Organic FeFETs may be therefore be less suitable for high-density memory applications but they may turn out to be the best solution for low-cost large-area applications based on integrated circuits of organic transistors because the device structure and processing technology of the organic transistors are similar to those of the FeFETs. The first integrated memory circuits based on organic FeFETs that were made with printing techniques have recently been demonstrated.^[83]

High field-effect mobilities were obtained in FeFETs by creating a smooth interface with a high mobility polymer semiconductor. The mobility can potentially be improved further with small molecule semiconductors but this approach has encountered difficulties associated with the high interface roughness of P(VDF-TrFE). The surface topography problem can perhaps be solved by combining vapor-deposited small molecule semiconductors and ferroelectric oligomers.

It was found that FeFETs using unipolar (p-type) semiconductors depolarize when they are brought into the off-state because the semiconductor is unable to supply compensation charges when the FeFET is in the off-state. This depolarization may have adverse effects on the retention performance, but this has not yet been confirmed experimentally. Ambipolar semiconductors can effectively avoid this problem because they can supply compensation charges to the ferroelectric in both polarization states. Not much work has been done yet on ambipolar organic FeFETs. A major challenge for ambipolar FeFETs is to retain a current bistability that is high enough for memory applications. Achieving this goal will probably require tuning of the p- and n-type behavior of the semiconductor material.

Further applications for FeFETs can perhaps be found outside the area of memory devices. It has already been demonstrated that polymer FeFETs can be used for sensor applications such as infrared detection.^[87,88] Another report showed that a

P(VDF-TrFE) gate dielectric can attenuate the magnetic response of a ferromagnetic semiconductor in an organic/inorganic hybrid FeFET.^[89] This achievement could lead to the development of novel memory elements and spintronic logic elements.

Ferroelectric diodes based on phase-separated blend are perhaps the most promising device concept as they combine the favorable characteristics of capacitors and FeFETs, i.e., resistive switching and a simple device geometry and rectification that facilitates the integration into a larger array of memory bits. To demonstrate the full potential of this concept more fundamental research needs to be done. High-density cross-point memory arrays are being developed. The challenge is to further characterize the switching mechanism and to reduce the size of the phase separation.

Application of organic memories is typically envisaged for system in foil applications. Examples range from contactless RFID transponders (electronic barcodes, smart tags), through to integrated drivers for flexible displays and electronic paper, to textile integrated electronics. The attractive features of polymers include solution processing by spin coating or inkjet printing on large area foils and the possibility of molecular design through chemical synthesis. Each system in foil application has specific requirements on key memory parameters such as cell size, programming cycle endurance, data retention and read/write times. Due to the lack of a wired power supply RFID tags should operate at low power, while solid state data storage asks for small cell size and fast access. Apart from ferroelectric capacitors for low-end data storage all envisaged applications are still in a research phase.

The comparison in Table 1 between ferroelectric diodes and metal–organic semiconductor–metal junctions shows that both concepts currently offer a similar performance level. However, many implementations of the junction-concept have the disadvantage that their memory functionality relies on the formation of filaments, as demonstrated by Cölle et al.^[85] Due to a lack of control on the size and the positioning of the filaments they will form a limitation on the minimum lateral dimensions of a memory device. In a recent review Scott and Bozano have argued that there is currently a substantial lack of understanding of the mechanisms involved to make the junctions work, which

impedes their further development.^[6] The role of an oxide at the metal–polymer interface in the junctions and the memory switching speed of the junctions are the subject of further debate.^[90,91] The switching mechanism of ferroelectric diodes require further basic research as well but it has been demonstrated that the origin lies in the ferroelectric response of P(VDF-TrFE). The minimum lateral dimensions of diodes are determined by phase separation, which is a well known process that can be manipulated using solvent choice, materials choice, temperature, atmosphere, etc. The understanding of the switching mechanism and phase separation in ferroelectric diodes will facilitate future developments.

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