Recent Development in Polymer Ferroelectric Field Effect Transistor Memory

Youn Jung Park, Hee June Jeong, Jiyoun Chang, Seok Ju Kang, and Cheolmin Park

Abstract—**The article presents the recent research development in polymer ferroelectric non-volatile memory. A brief overview is given of the history of ferroelectric memory and device architectures based on inorganic ferroelectric materials. Particular emphasis is made on device elements such as metal/ferroelectric/metal type capacitor, metal-ferroelectric-insulator-semiconductor (MFIS) and ferroelectric field effect transistor (FeFET) with ferroelectric poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE). In addition, various material and process issues for realization of polymer ferroelectric non-volatile memory are discussed, including the control of crystal polymorphs, film thickness, crystallization and crystal orientation and the unconventional patterning techniques.**

Index Terms—**Polymer ferroelectrics, non-volatile memory, PVDF, P(VDF-TrFE), capacitor, MFIS, FeFET**

I. INTRODUCTION

The recent unprecedented development of portable computing, information management, and communications grows the demand for technologies enabling the rapid manipulation, caching, and storage of large amounts of data. Many of these applications require convenience, speed, energy efficiency, affordability, and reliability. There are several current technologies providing some form of nonvolatile random-access-memory (NV-RAM) data storage to meet these needs. Currently, the most widely used nonvolatile NV-RAM technology is Flash, a charge-storage technology that can achieve relatively high density at low cost because it is based on standard silicon integrated-circuit technology. The main drawbacks of Flash memories are low speed, cycle energy usage, and limited cycle life. Other candidate NV-RAM technologies currently under consideration include magnetic (MRAM), phase change (OUM), resistive (RRAM), and ferroelectric (FRAM) [1,2]. In this article, we review the recent development in non-volatile memory based on ferroelectric materials. In particular the focus will be made on the important memory elements such as ferroelectric capacitor, metal/ferroelectric/insulator/semiconductor (MFIS) and ferroelectric field effect transistor (FeFET) based on polymer ferroelectrics. Next brief overview of the mechanism of ferroelectric switching, the device structure and the development of inorganic ferroelectric memories is given.

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II. FERROELECTRIC SWITCHING

A ferroelectric crystal maintains a permanent electric polarization that can be repeatedly switched between two stable states by an external electric field, thus exhibiting a polarization–electric-field-hysteresis loop, analogous to the magnetization–magnetic-field-hysteresis loop exhibited by ferromagnetic crystals. In addition, like magnetic materials, ferroelectric crystals can form domains, each with a unique polarization axis. The hysteresis loops are characterized by the magnitude

of the zero-field remanent polarization after saturation with a large electric field and by the magnitude of the coercive field E_c, the minimum value of the electric field necessary to reverse, or switch, the polarization state.

III. Ferroelectric Memory Structures

Early work for NV-RAM based on ferroelectrics was done with thin films of ferroelectric perovskite oxides, which show two stable polarization states at zero bias, designated as 0 and 1 states [2]. Memory function is performed by electrically switching between the two states in a ferroelectric capacitor device structure, which involves a destructive readout. Loss of written data at one polarization state in a readout operation requires restoration by a rewriting cycle, which increases access time, limits operational life, and enhances memory cell area to accommodate the additional circuitry [3,4].

Ferroelectric memory integrated with silicon CMOS was demonstrated in 1987. The initial ferroelectric memory test chip consisted of only 256 bits; each bit contained two $PbZr_{0.5}Ti_{0.5}O_3$ (PZT) capacitors that formed a nonvolatile shadow RAM for the accompanying six-transistor static random access memory cell (6T SRAM) [5]. Mass production of FRAM products commenced in 1992 after the development of a 4 kbyte memory that utilized a high reliability two transistor, two-capacitor (2T2C) cell that was more area efficient than the early shadow RAM cells [6,7]. Since 1992, there has been an exponential growth in FRAM capacity to a current maximum of 64 Mbytes and an exponential decrease in the integrated CMOS transistor gate length to 0.13 μm. Many other alternatives to PZT that were investigated include $SrBi_2Ta_2O_9$ (SBT), $(BiLa)_4Ti_3O_{12}$, $BaMgF_4$, $Bi_4Ti_3O_{12}$, and $Pb_5Ge_3O_{11}$. The objective was to find a ferroelectric material that showed little or no degradation of the switchable ferroelectric polarization while cycling the bit capacitor structure through typical read and write operations. The SBT-based products are currently limited to low memory capacity (less than 16 kbytes) smartcard applications, although test chips with capacity as high as 4 Mbytes have been demonstrated [8]. In 2T2C devices as shown in Fig 1a, the ferroelectric capacitors are formed on top of a field oxide such that the capacitors are next to the accompanying transistors

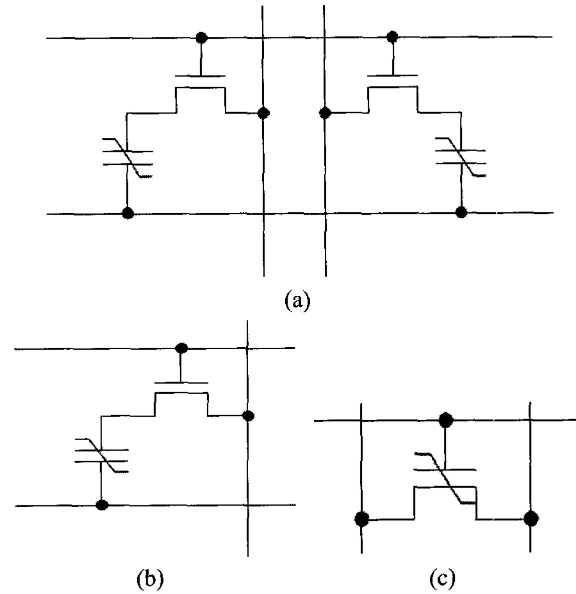

Fig. 1. Ferroelectric memory cell structure (a)2T/2C (b)1T/1C (c)1T.

and each component of the cell occupies a uniquely defined area. This architecture is referred to as the capacitor-over-field-oxide (COFO) architecture and it results in a relatively large $60F^2$ (F is the metal half-pitch) cell size.

If a switching charge pulse is detected from the capacitor of the one-transistor, one capacitor (1T1C) cell, the cell capacitor is said to be in the 1 state, whereas if no switching charge is detected, the cell capacitor is in the 0 state. Because of the success of FRAM mass production and the potential for a variety of stand-alone and embedded applications, several manufacturers have focused development on continued scaling of FRAM to achieve higher capacity and higher density. As part of the scaling effort, the FRAM cell has undergone an additional change in architecture to reduce cell size. A cell factor decrease is achieved by building the ferroelectric capacitor on top of a plug that contacts an underlying access transistor. For the capacitor-on-plug (COP) architecture, a cell size of $18F^2$ was achieved and it was used to demonstrate 4 and 64 Mbyte memories [9,10].

An approach for circumventing the intrinsic limitations of 2T2C and 1T1C type memories to read/write endurance and memory unit cell size was to employ a nondestructive readout of the nonvolatile ferroelectric capacitor polarization state. Initial FRAM designs had relied on a destructive readout (DRO) scheme where the polarization state of the memory bit

had to be switched in order to sense the stored memory state. Once the bit was read, the memory state was rewritten into the ferroelectric capacitor by resetting the polarization. Switching the polarization during both write and read operations caused reduced endurance. Since many memory applications require more read accesses than writes, a nondestructive readout (NDRO) of the ferroelectric capacitor would necessarily increase endurance.

IV. Ferroelectric Field Effect Transistor Memory

For nonvolatile memory with a nondestructive readout capability and a smaller cell size, a memory structure based on metalferroelectric-semiconductor field-effect transistor (MFESFET) is more promising. Ferroelectric thin films are required as gate dielectric to form a ferroelectric field-effect transistor (FE-FET) device structure as shown in Fig 1c[11,12]. The polarization state of the ferroelectric gate set by the polarity of the writing gate voltage controls the electrical conductance of the channel over the Si surface and thus distinguishes two logic states, the On or Off states of the channel current for memory function [13,14]. Because spontaneous polarization directly controls channel conductance, neither the ferroelectric cell capacitance nor the requirement of a high polarization are determining factors in the device operation. Thus, in addition to random access, FeFET has a potential for high density (1T structure per cell), low-power consumption, and high speed in comparison to Flash memories. Fabricating FeFET involves the integration of ferroelectric films directly over the FET channel of a Si metal-oxide-semiconductor field-effect transistor (MOSFET) device [15].

Two important electrical characterization methods for the development of MFIS and FeFET are shown in Fig. 2a and b, respectively. A prominent feature in a *C-V* curve of a MFIS diode is a hysteretic behavior which arises from the ferroelectric material. Because uncompensated traps at the insulator/ semiconductor interface can also lead to hysteric *C-V* curves carefully performed measurements are mandatory for attributing a hysteresis in a *C-V* curve unambiguously to ferroelectricity. A necessary but not commensurate

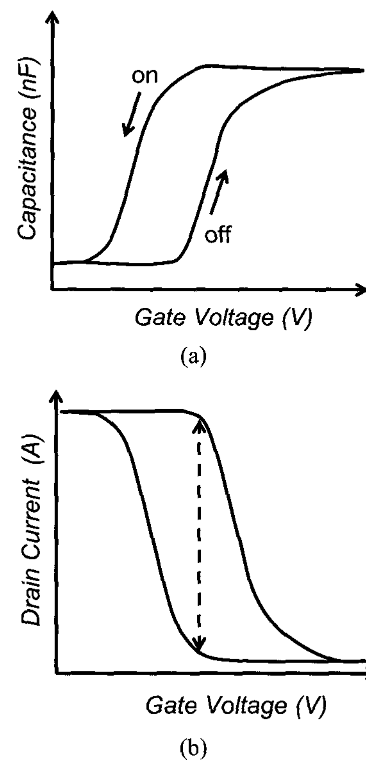

Fig. 2. Schematic plot of ferroelectric memory characteristics (a) Capacitance-Voltage data for the MFIS capacitor (b) Drain current hysteresis with voltage sweep in a ferroelectric field effect transistor.

condition is a clockwise cycle of the hysteresis. The hysteresis of the *C-V* curve reappears in the source-drain current versus gate voltage curve, as shown in Fig. 2a. The maximum voltage width of the hysteresis is defined as the memory window, one of the most important parameters of a FeFET. A possible readout voltage to distinguish the two possible states is also shown in Fig. 2b.

V. Inorganic FeFETs

The idea of the FeFET, presented in a patent in 1957 [16], was first realized by Moll and Tarui in 1963 [17], with triglycine sulphate (TGS) on a CdS substrate and implemented on silicon by Wu in 1974 [18]. A number of perovskite ferroelectric oxides, such as $SrBi_2Ta_2O_5$ and $PbsZrTidO_3$, have been studied in the past. In an ideal FeFET the ferroelectric is in *direct* contact with the drain-source channel of the transistor. The ferroelectric is an active part of the transistor and the FeFET is a single device. The performance of the FeFET is therefore inextricably connected to its

interface physics and the electronic properties of this interface. The interface is one of the most serious problems for the FeFET. The transistor properties such as threshold voltage, saturation voltage, or the *C-V* curve of the gate stack are strongly influenced by localized states (e.g., dangling bonds) and impurities at the interface. Interdiffusion between the ferroelectric and Si is another bottleneck for the FeFET.

Essential challenges for the FeFET are the improvement of the retention time and the suppression of serious parasitic effects such as the charge traps at the Si-ferroelectric interface. The problem of short retention times in FeFETs is believed to arise from the fact that the finite depolarization field due to the a noncomplete charge compensation at the semiconductor side of the ferroelectric may lead to the formation of 180° domains or to current injection, both of which reduce the polarization in the ferroelectric film and consequently lead to information loss. One possible solution in the case of a FeFET is to incorporate one insulating buffer layer between the Si and the ferroelectric to have a metal-ferroelectric-insulator-silicon (MFIS) structure [19,20]. Several buffer layers, for example, SiO_2, CeO_x, and Si_3N_4, have been investigated. The most recent works by using alternative gate oxides such as HfO_2 or HfAlO show encouraging results. The retention time for the gate layer sequence Pt/SBT/HfO_2 /Si was 30 days, the best value observed up to now [19,21]. Beside a low density of interface states the band offset between Si and the ferroelectric or the buffer needs to be sufficiently large to avoid electron injection during programming. The consequence is again a low retention time. Even more complex gate sequences have been investigated in the form of metal-ferroelectric-metal-insulator-silicon (MFMIS) structures [22]. The technological advantage here is that in this case optimized MFM fabrication from FRAMs is used. To control the source-drain current of a field effect transistor a simulation showed that materials with a low P_r (~2 μC/cm^2) are optimal. Since typical complex oxide ferroelectrics often exhibit more than ten times higher P_r, subloops are used to obtain sufficiently low P_r values and in addition to avoid electric breakdown of the buffer. Polymer ferroelectrics in general with relatively low P_r and high bandgap are, therefore, attractive for FeFET type non-volatile memory as shown next.

VI. POLYMER FEFETS

Organic ferroelectric polymers are worth exploring as an alternative to perovskite ceramics. Polymers are chemically inert to Si and could be easily processed as thin films at relatively lower temperatures (< 200°C) by solution-based techniques, which to a large extent addresses present concerns about stability of the Si-ferroelectric gate interface. Extensive studies of the crystalline structure and ferroelectric properties of the thin films of a number of polymers, polyvinylidene fluoride (PVDF) [23,24], nylon-11 [25], and polyurea [26] have been reported, which show considerable promise in this direction. Compared to most ferroelectric ceramic oxides, low dielectric constant (~$13.8\varepsilon_o$) of PVDF copolymer permits the use of SiO_2 as a buffer layer ($\varepsilon_{Si} = 3.9\ \varepsilon_o$) without encountering large depolarization fields. Further, unlike ceramic ferroelectric structures, the integrity of ferroelectric polymer/SiO_2 /Si interfaces is no longer an issue. In addition, the polymer ferroelectrics are conveniently combined with organic semiconductors such as pentacene, poly(3-hexylthiopene) (P3HT) and so on in the case of FeFET devices.

VII. FERROELECTRIC POLYMERS

Both piezoelectricity and pyroelectricity were observed over 30 years ago in PVDF. Piezoelectric transducers made by solvent casting were soon commercially available, though it took a decade to establish that ferroelectricity was the origin of these effects in PVDF. Synthesis of PVDF and its copolymers has been standardized and is thoroughly described in the texts edited by Wang *et al.* [27] and Nalwa [28], and in several review articles [29–31]. PVDF is the most widely used ferroelectric polymer and is manufactured in large quantities for a wide variety of applications, ranging from protective coatings to ultrasound transducers. Though PVDF shows clear repeatable polarization hysteresis, there was doubt initially that this was of ferroelectric origin because many polymers exhibit long-lived but transient hysteresis due to either charge injection or induced polarization. Either of these

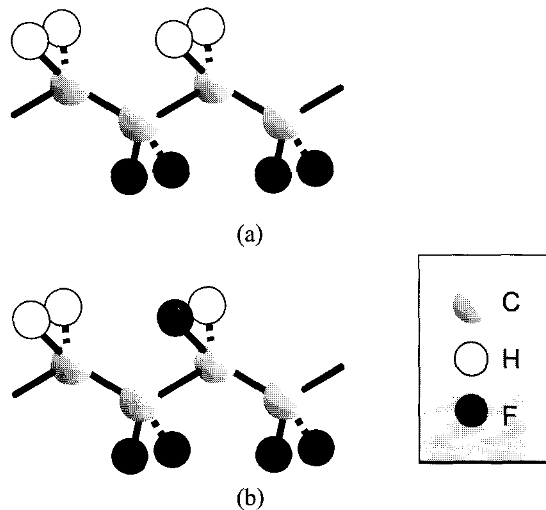

Fig. 3. Molecular structure of ferroelectric polymer (a)PVDF (b)P(VDF-TrFE).

mechanisms produces electrets, which exhibit metastable piezoelectric and pyroelectric effects that can persist for hours, days, or even years. Direct evidence of ferroelectricity was first provided by X-ray diffraction studies [32] and unambiguous evidence that hysteresis was due to switching between opposing but equivalent polarization states came from the synthesis and systematic study of the copolymers with TrFE [33] and tetrafluoroetylene (TeFE) [34]. The substitution of either TrFE or TeFE suppresses the ferroelectric–paraelectric phase-transition temperature below the melting point, thus providing a direct connection between the switching charge and the appearance of spontaneous polarization.

The molecular units in the polymer chains of PVDF and P(VDF-TrFE) have net dipole moments pointing from the electronegative fluorine to the electropositive hydrogen, as shown in Fig. 3. These chains can crystallize in parallel rows and, in the ferroelectric state, the dipoles of all chains are aligned along a twofold crystalline axis, resulting in a macroscopic polarization. Switching is accomplished by applying a large electric field opposing to the polarization. The main advantages of ferroelectric polymers relative to perovskites are the low production costs, ease and flexibility of fabrication in a variety of thin-film forms, chemical stability, and resistance to degradation caused by strain or defects. The disadvantages of the polymers are on the other hand their relatively low melting point (150 °C–200 °C), low stiffness, and the polymorphous structure.

VIII. Thin Film Fabrication of Ferroelectric Polymers

One of the major advantages of the ferroelectric polymers is their solution compatibility with common organic solvents and thus memory unit capacitors or transistors are easily achieved by a simple spin-casting process. The polymer is first dissolved in an organic solvent at concentrations of a few weight percent. The solution is then formed into sheets or films by casting or spinning and the solvent evaporated, leaving a pliable solid sample that is typically polymorphous—an inhomogeneous mixture of amorphous and crystalline material.

Another notable innovation by a group at Kyoto University is the growth by epitaxial vapor deposition of crystalline mats of VDF oligomers consisting of short iodine-terminated chains of VDF with the chemical formula $CF_3-[CH_2-CF_2]_{17}-I$ [35, 36]. The oligomer films are likely ferroelectric as they exhibit reversible switching. The oligomer films are promising alternatives to PVDF or its copolymers, but relatively little is known about their behavior. The oligomers are appealing for several reasons. 1) They have the same basic conformational structure as PVDF. 2) They are easily deposited by evaporation. 3) As monodispersed molecules, they crystallize more readily and should have fewer chain-folding defects and lamellar structures than those that are prevalent in PVDF and its copolymers. Thin PVDF films were also fabricated by a low-pressure chemical vapor polymerization process which involves polymerization of an isotropic vinylidene fluoride monomer condensate layer by cleavage of C double bonds using $:CF_2$ initiators derived from hot-filament, thermochemical decomposition of the hexafluoropropylene oxide C_3F_6O. The method is beneficial because of its compatibility with sub-micrometer semiconductor device fabrication [37].

Two dimensional polymer ferroelectric films were successfully fabricated by Langmuir-Blodgett deposition which allowed systematic control of the film thickness by the number of the sequential layer deposition. The films show excellent crystalline and orientational order with the first order ferroelectric-paraelectric transition. All *trans* polymer conformational order was achieved by the method and in turn attributed

to the excellent ferroelectric properties even in a 10 Å thick film [38].

IX. Recent Development in Polymer Ferroelectric Memories

1. Metal/Ferroelectric Polymer/Metal Capacitor

In order to fabricate a device with low voltage switching below 20 V, the film thickness of PVDF and its copolymer with TrFE should be less than 200 nm due to its high coercive field (E_c) of approximately 50 MV/m. Various properties of metal/ferroelectric thin film/metal (MFM) capacitors have been recently examined including the work function of electrodes, frequency dependent fatigue, thermal history and ferroelectric polymer/metal interface and so on [39-41]. The asymmetric polarization switching frequently observed in a capacitor arises from the work function difference of the metal electrodes and the degree of asymmetry increases with the increasing work function difference. In addition, it is found that the polarization switching becomes much faster for a sample with high work function metals such as Ni [39]. Another interesting result is the frequency dependence of a metal/P(VDF-TrFE)/metal capacitor in which the driving voltages with lower frequency and higher amplitude correspond to higher fatigue rates. Zhu *et al.* have proposed a universal scaling behavior with N/f, where N is the number of switching cycles and f is the frequency in the fatigue behavior originating from the trapped charges, injected from electrodes into polymer films [40].

In order to adopt the polymer ferroelectrics into the current integrated process which requires high temperature well above T_m, the ferroelectric properties become more important, depending on thermal history from melt-recrystallization. In addition, it is critical issue for the fabrication and operation of a device whether or not the properties are reversible below and above T_m. We have recently investigated the effect of thermal treatment of thin P(VDF-TrFE) films on ferroelectric properties. The improved remnant polarization observed in the samples annealed at temperatures between T_c and T_m completely disappears

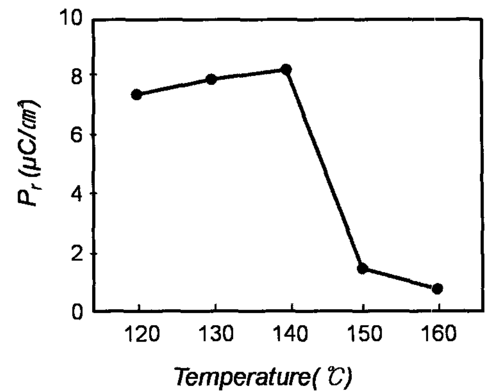

Fig. 4. Polarization behaviors with heat treatment temperatures presenting the thermal stability of ferroelectric polymer capacitors.

when the samples are heated above T_m and re-crystallized through various pathways as shown in Fig 4. Extinction of the remnant polarization of the melt-recrystallized samples arises from the modification of the molecular chain orientation upon recrystallization presumably due to the preferential crystal face interaction to the electrode surface. The molecular chain *c*-axis and polar *b*-axis are preferentially oriented perpendicular and parallel to the electrode surface, respectively, causing the effective electric field to the ferroelectric microdomains to be almost zero [41].

The interface between metal electrode and ferroelectric polymer has been of great interest due to its significant influence on MFM capacitor performance. We employed a topographical metallic substrate based on etched Al as a bottom electrode of a ferroelectric capacitor and observed facile recovery of ferroelectric polarization after high temperature annealing in a P(VDF-TrFE) thin film on an etched Al bottom electrode which has a topographically nanostructured surface with hexagonal registry of the recessed hemi-spherical bowls of approximately 100 nm diameter as shown in Fig 5. Fairly large remanent polarization of 10μC/cm^2 was obtained after annealing up to 185 °C with the etched Al electrode while the polarization rapidly dropped near the melting temperature of P(VDF-TrFE) (~150 °C) with a flat Al electrode [43]. Not only the topographical substrate but also chemically modified surfaces with self assembled monolayers (SAMs) have been utilized for controlling the capacitor performance. Depending on the polarity of the chemical surface, molecular orientation of P(VDF-TrFE) was significantly

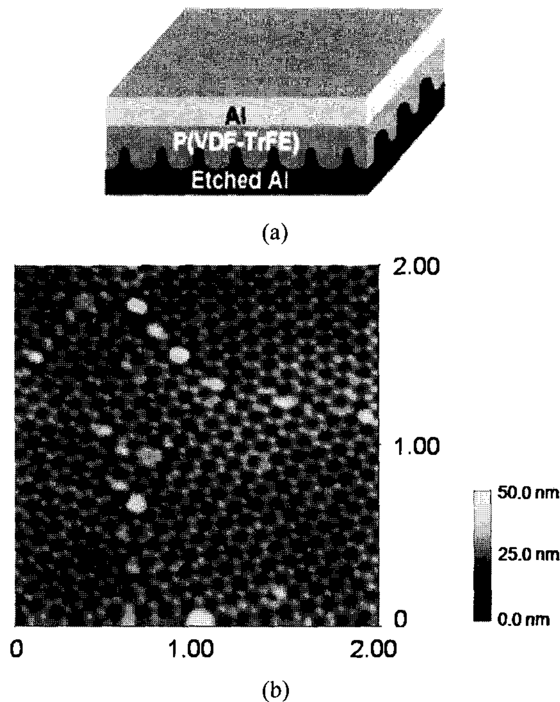

Fig. 5. The employment of topographic patterned bottom electrode (a) Scheme of P(VDF-TrFE) capacitor with etched Al (b) Top view of an etched Al electrode from a tapping mode atomic force microscopy [43].

altered, which in turn leads to the different polarization behavior [44]. Another intriguing demonstration for controlling the interface is to employ a polymeric conducting layer of thin polypyrrole-poly(styrene sulfonate) acid (Ppy-PSSH) film as interface layers between both bottom and top metal electrodes. Xu *et al.* observed that a capacitor with the sandwiched structure Ti/Ppy-PSSH/P(VDF-TrFE)/Ppy-PSSH/Ti shows prominent ferroelectric properties with the coercive voltage and the remanent polarization of 2.6 V and 86 mC/m^2, respectively. The improved device performance arises from the increased crystallinity as well as the enhanced crystal dipole orientation [42].

2. Metal/Ferroelectric Polymer/Insulator/Semiconductor (MFIS) and FeFET

A potential nonvolatile bistable capacitor memory element consisting of metal/P(VDF-TrFE)/silicon-oxide/n-type silicon semiconductor has been demonstrated, combined with Langmuir-Blodgett film process for deposition of highly ordered P(VDF-TrFE) thin film. A clear capacitance hysteresis was observed as the gate voltage was cycled between +25 V with a capacitance dynamic range of 8:1 [45]. The MFIS device also exhibits the threshold voltage shift of 2.8V on SiO_2 insulator ineffective for non-volatile memory application at zero gate voltage. More extensive and detailed study was performed by Lim *et al.* of the electrical properties of MFIS using SiO_2 insulator and P(VDF-TrFE). They have observed that the (*C–V*) hysteresis and bidirectional flatband voltage shift at −10 to +6 V, depending on the polarization field direction and remnant polarization at the ferroelectric PVDF copolymer gate, presents a memory window [15]. In particular, the observed asymmetry of the negative flatband-voltage shifts in the negatively poled ferroelectric polymer state results from the depletion layer formation, which reduces the field across the polymeric gate. Internal field due to negative and positive bound charges within PVDF copolymer and SiO_2, respectively, influences polarization switching by pinning of dipoles. Fujisaki *et al.* have recently demonstrated that the intrinsic negative flatband-voltage shift on SiO_2 insulator observed in the previous works is largely eliminated by employing an interlayer of a 3 nm thick Ta_2O_5. Rectangular-shaped capacitance-voltage hysteresis loops were obtained with a voltage sweep range narrower than 5V. The maximum memory width was 4.7V [46].

Organic field-effect transistors are ideally suited for low-cost, low-performance logic circuit applications on flexible substrates. Recently, FeFETs with organic active layers have been demonstrated, invariably with the use of evaporated pentacene as the semiconductor material. Schroeder *et al.* utilized nylon poly(m-xylylene adipamide) (MXD6) as a ferroelectric gate dielectric in a pentacene FeFET and demonstrated an on/off ratio of 200 at 2.5 V gate bias, 30 at zero gate bias and a retention time of three hours [47]. The programming time, estimated from the reported ferroelectric switching current duration, exceeds 200 ms. Unlike the most of ferroelectric polymers including PVDF and P(VDF-TrFE), MXD6 exhibits ferroelectric properties in its amorphous state which may be potentially beneficial for scalibility of memory unit cells. Unni *et al.* also obtained a similar on/off ratio and retention time from a pentacene FeFET based on P(VDF-TrFE). In spite of the interesting memory

properties observed, both reports do not successfully prove that the memory functionality is driven by ferroelectricity and not by a secondary effect such as charge trapping [48]. This would have been demonstrated by, for example, a sudden rise in the drain current when the gate field reached the coercive field of the ferroelectric insulator layer. In fact the gate field applied in the transfer curve measurement by Unni *et al.* is much lower than the coercive field of their ferroelectric material. Matsuo *et al.* have reported the expected drain current increase at around the coercive voltage and a data retention time of a week, but the on- and off-states after this time differ only by a factor of 0.5 [49].

High-performance solution-processed polymer FeFETs have been demonstrated by Naber *et al.* consisting of a P(VDF/TrFE) ferroelectric copolymer as gate insulator and poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylene-vinylene] (MEH-PPV) as a semiconductor [50]. The polymer FeFETs have a remanent On/Off ratio of several orders of magnitude at zero gate bias, a long data retention time, a high programming cycle endurance and a short programming time. The high on/off ratio mainly originates from the large on-current in the semiconducting channel which is indicative of a large surface charge density ρ of 18 mC/m^2. which is one quarter of the remanent polarization of the ferroelectric. The same group has also fabricated an organic FeFET memory with thin solution processed P(VDF-TrFE) gate dielectric that has programming voltage of 15 V with 3 hour retention capabilities [51]. An optimized P(VDF-TrFE) film formation using cyclohexanone as a solvent was a key factor for the successful device.

A solution processed composite film of P(VDF-TrFE) and barium titanate (BT) has been also utilized as a gate dielectric layer in an organic FeFET with regioregular poly(3-hexylthiophene) (rr-P3HT) semiconductor. Yildirim *et al.* argued that the composite films exhibited high specific volume resistivities combined with dielectric constants of up to 51.5 at 1 kHz and the FeFET fabricated operated at relatively low voltage with good memory retention [52]. The device properties demonstrated, however, seem to be questionable to justify the authors' claims properly. A top gate ZnO FeFET has been reported by Noh *et al.* with a poly

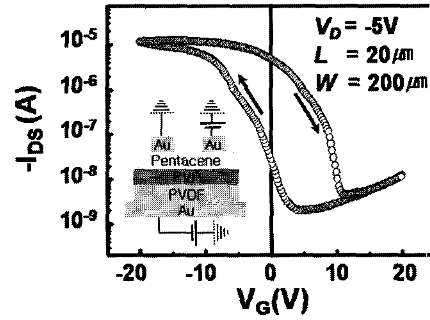

Fig. 6. I_D-V_G transfer curve of pentacene OTFT with bilayered PVDF–PVP gate dielectric. The hysteresis direction is indicated with the arrow and the inset depicts the FeFET device structure [54].

(4vinylphenol) (PVP)/P(VDF-TrFE) double layer gate dielectric which shows remarkably reduced leakage current with the aid of the PVP buffer. The device exhibits a field effect mobility of 0.36 cm^2/V and a large memory hysteresis in the transfer characteristics with the data retention longer than 2 hours [53].

We have recently described a method to fabricating a FeFET based on ferroelectric β-type PVDF thin films on Au substrate by the humidity controlled spin casting combined with rapid thermal treatment. Our device with the β-PVDF has much higher thermal stability up to 160 °C than P(VDF-TrFE). A FeFET fabricated also shows a drain current bistablility of 100 at zero gate voltage with ±20V gate voltage sweep as shown in Fig 6 [54].

X. Challenges for Material Design

1. Polymorphic Crystals of PVDF

The ferroelectric crystallites usually have hierarchical structures with the characteristic lamellar morphology made of chain folding. The typical dimensions of the lamellae are of order 50 nm × 500 nm × 5 μm with the chains parallel to the shortest dimension. The lamellae are microscopically ferroelectric, with in-plane polarization. The sequential configuration order of monomeric unit of the polymers is a prime factor for synchronized collective conformational rotation absolutely necessary for optimized switching of the permanent dipole guaranteeing maximum polarization and minimum electric field. For example, consecutive trans configuration, i.e. TTTT sequence provides a good polarization while alternating trans and guache

configuration, i.e. $TGT\overline{G}$ one leads to almost null polarization due to internal cancellation of dipole ordering. Another configuration which imparts to relatively weak ferroelectric polarization is one with TTTG sequence. Several crystalline structures induced by the regular chain packing of the different configuration orders are found in PVDF known as α, β, and γ which correspond to $TGT\overline{G}$, TTTT and TTTG, respectively. Successful development of ferroelectric polymer devices, therefore, depends on how effectively to fabricate polar ferroelectric crystalline structures such as β, and γ. In the case of copolymers with TrFE, the delicate configuration balance provided by addition of one more fluorine atom in the backbone always gives rise to polar ferroelectric β structure. There have been a number of papers that discuss the crystallization and the polymorphic changes of PVDF films prepared either from melting or by solution. Most of works have focused on methods to achieving polar β structure in several micron thick films that are rarely applicable for memory device due to substantially high operating voltage of more than 100 V. The methods include mechanical stretching, high compression, hygroscopic salts and rate of cooling and heating, solvent evaporation [54]. One should, therefore, find a way based on spin casting process to fabricate polar ferroelectric thin PVDF films of less than 200 nm in thickness that are suitable for reasonably low operating voltage of approximately 10 V. A recent work by Wang *et al.* has proposed a method for fabricating ultra thin melt-drawn film with β crystals by melting and re-crystallization under carbon evaporated surface [55]. From the industrial point of view, spin coating is one of the most desirable methods for large area uniform film formation and thus provides a great benefit when it is incorporated in fabricating PVDF based devices. Our recent work has also shown PVDF thin films with polar γ crystals prepared by pressurizing *spin cast* thin films at certain temperature range [56]. It is still challenging to conveniently prepare uniform ferroelectric PVDF thin film with *β crystals* whose permanent polarization can switch at low voltage with high temperature stability. Our recent report suggests a practical way for fabricating ferroelectric thin PVDF films spin cast on Au substrate mostly with β crystals by the rapid thermal annealing at 150 °C following the spin coating under controlled humidity [54].

2. Thickness Effect on Ferroelectric Polarization

Most of the earlier works on polymer ferroelectric films have been focused on PVDF and also copolymers with TrFE with thickness of 10 μm or more. However, since those ferroelectric polymer films have been proposed for nonvolatile memory elements, it is indispensable to reduce film thickness due to the relatively high coercive field (E_c) of 50MV/m for P(VDF-TrFE) to attain lower operation of voltage. A number of studies have dealt with a reduced-dimension system in spin cast ferroelectric layers and found a significant decrease of remanent polarization and crystallinity of the copolymer of VDF and TrFE as the film thickness decreased. Naber *et al.* overviewed the relationship between layer thickness and remanent polarization in spin cast P(VDF-TrFE) capacitors, including their results, as a summary from the literature regarding the thickness scaling [51]. Even though all the processing conditions for those plotted data are not the same, the abrupt decline of the remanent polarization measured in sub-100nm P(VDF-TrFE) films has been shown in Fig 7 and this behavior is attributed to the decrease of crystallinity in P(VDF-TrFE) thin films in most works. In the ultrathin film below 100nm, it is figured out that the crystallinity diminishes due to the strong interaction between substrate and ferroelectric polymer.

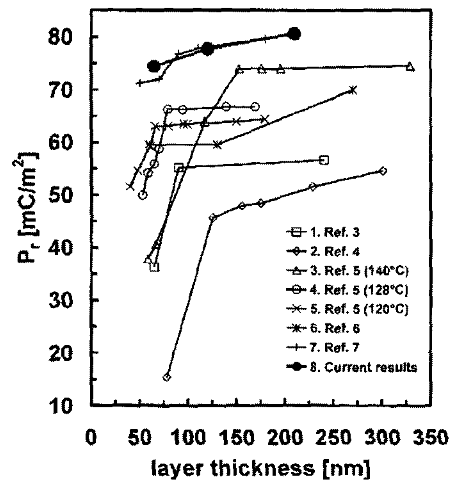

Fig. 7. Dependence of remanent polarization with the variation of layer thickness measured in the literature [51].

However, a few works have found the improvement of polarization in ultrathin film recently and shown low voltage operation of ferroelectric capacitors. Naber *et al.* demonstrated that the remanent polarization of 6.5μC/cm^2 in P(VDF-TrFE) 65nm film capacitor is switched with 5.2V, with the employment of a conductive polymer as the bottom electrode material [51]. Similar ferroelectric and switching behavior was observed by Xu. *et al.* in the sandwiched structure Ti/Ppy-PSSH/P(VDF-TrFE)/Ppy-PSSH/Ti where ferroelectric polymer layer is approximately 50nm, with E_c as low as 2.6V and P_r of 8.6 μC/cm^2 as mentioned previously [42]. More challenging result was published in the work done by Ishwara and his coworkers. They fabricated 60nm-thick P(VDF-TrFE) thin film capacitors with P_r of 11.9 μC/cm^2 and E_c of 2V and metal-ferroelectric-insulator-semiconductor diodes with 100nm-thick P(VDF-TrFE) films [46]. When LB method was applied which allowed highly ordered P(VDF-TrFE) molecular chain orientation, even approximately 1 nm thick film exhibited ferroelectric polarization.

3. Control of Crystal Orientation

Effective crystal orientation with respect to electric field direction is also of a prime importance for successful device realization. For PVDF and P(VDF-TrFE), the polarization is optimized when the crystal *b* axis becomes parallel to electric field. The abrupt reduction of polarization in spin cast thin P(VDF-TrFE) films with sub 100nm can be attributed not only to the decrease of crystallinity, but also to the ineffective orientation of polymer crystals. The critical impact of crystal orientation on the polymer ferroelectrics is shown in the literature by Bune *et al.* where ferroelectric properties were measured even in films of only two monolayers, fabricated by the LB technique [38]. We have also addressed the extinction of ferroelectric polarization arising from the rotation of polymer crystals to *c* axis parallel to surface normal upon melting and re-crystallization [41]. The crystal orientation dependent polarization was also investigated in Al/P(VDF-TrFE)/Au capacitors in which Au bottom electrode was treated with SAMs for controlling chemical nature of surface. In general a preferred crystal orientation observed on surfaces with polar nature is found to provide superior polarization [44].

4. Patterning of Ferroelectric Polymers

Another important requirement for realizing polymeric memory devices is the capability of micro/nano pattern formation to ensure high density integration per unit area. The selective etching of material using a patterned mask is common in CMOS based memory fabrication. Ferroelectric polymer, however, is significantly damaged or alters its intrinsic properties under the harsh patterning conditions, which suggests that a new non-destructive pattern technique should be applied.

Soft lithography is one of highly plausible alternatives. Recently Hu *et al.* have fabricated nanometer scale patterns of PVDF using nano-imprinting lithography [57]. The confined crystallization and resulting molecular ordering of α type PVDF crystals was successfully demonstrated not only in the nanoscopic trenches produced by nano-imprinting but also in the nano-tubes of anodized aluminum oxide membrane. We also utilized capillary molding technique and reported micron scale pattern formation of PVDF with controlled crystal orientation. The previous works including ours [58], however, do not provide a practical patterning technique that produces isolated polar ferroelectric micro or nanodomains of PVDF because (1) the crystalline structure dealt with was non-polar α type and (2) some polymer remained on the imprinted regions, resulting in non-isolated patterned domains.

We have recently demonstrated a micro-patterning technique that produces patterned arrays of isolated ferroelectric γ type domains embedded into non-polar α structure in thin PVDF films [56]. The method is based on using micro-imprinting of a spin cast α type PVDF film. The localized regions pressed by a patterned PDMS mold turn into polar γ type structure under certain temperature and pressure We also reported that a capacitor fabricated with the pressed PVDF thin film showed reasonably high remnant polarization of approximately 6 μC/cm^2, with the coercive voltage of approximately 11 V. The localized polar ferroelectric domains are successfully scaled down to a few hundred nanometers as shown in Fig 8. Another work by Zhang

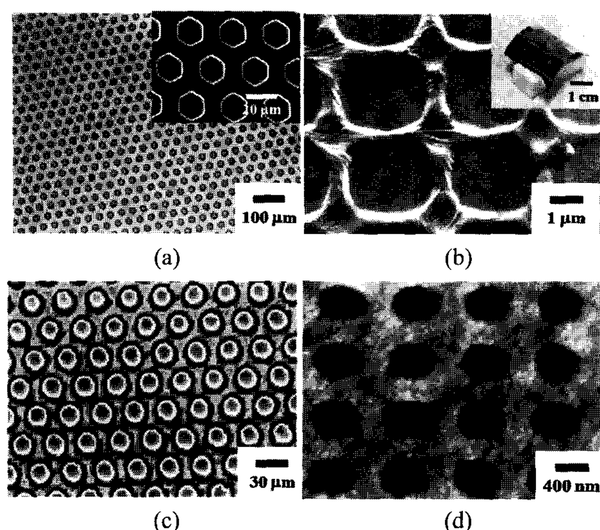

Fig. 8. The images from ferroelectric pattern arrays of PVDF films by microimprinting (a) the hexagonal holes (b) square pattern (c) 2D scanning IR images of a PVDF film (d) the PVDF pattern with circular posts of 400 nm diameter with isolated features [56].

et al. presents the optimal microimprinting conditions of P(VDF-TrFE) thin films for high remanent polarization and high poling-induced surface potential [59].

Direct writing by surface probe microscope is known as an efficient way to fabricate a nanometer scale pattern surface of PVDF and P(VDF-TrFE) [60]. In particular piezoresponse force microscope (PFM) has been used to manipulate and image polarization of ferroelectric polymer films, achieving polarization control with a resolution below 50 nm. This nanolithographic method is potential for high-density data storage and retrieval at densities exceeding 250 $Gbit/in^2$. Lateral modulation friction force microscope (LM-FFM) has been also useful not only for controlling the molecular orientation of P(VDF-TrFE) crystals but also potentially for nanopatterning the thin films. Localized friction by a surface probe tip at high temperature induced the reorganization of polymer chains along the field direction, giving rise to well ordered ferroelectric crystals.

XI. SUMMARY AND OUTLOOK

We attempted in this paper to describe the state of art in the field of polymer ferroelectric non-volatile memory. Starting with the overview of ferroelectric memory based on inorganic materials, we reviewed three main areas: metal/polymer ferroelectric/metal (MFM) capacitor, metal/polymer ferroelectric/insulator/ semiconductor (MFIS) and ferroelectric polymer field effect transistors (FeFET). In addition, various material and process issues for full realization of polymer ferroelectric memory were discussed including polymorphic crystals, film thickness, crystallization and crystal orientation and micropatterning process. Non-volatile memory based on ferroelectric polymers is promising by virtue of low cost, device flexibility, high performance and environmental compatibility. Numerous interesting questions are, at the same time, still open, for examples, reliability and scalibility and so on. Polymer ferroelectric memory will find its way for the emerging applications such as radio frequency identification (RFID) in organic electronics combined with printing technology near future.

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REFERENCES

[1] S. Ducharme, T. J. Reece, C. M. Othon, and R. K. Rannow, "Ferroelectric polymer Langmuire-Blodgett films for nonvolatile memory applications," *IEEE Transaction on Device and Materials Reliability*, vol. 5, no. 4, pp. 720-735, Dec. 2005.

[2] N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N.Y. Park, G. B. Stephenson, I. Stolitchnov, A.K. Taganstev, D.V. Taylor, T. Yamada, and S. Streiffer, "Ferroelectric thin films: review of materials, properties, and applications," *Journal of Applied Physics*, vol. 100, Sep. 2006.

[3] A. Sheikholeslami and P. G. Gulak, "A Survey of circuit innovations in ferroelectric random-access memories," *Proceedings of the IEEE*, vol. 88, no.

5, pp. 667-689, May 2000.

[4] T. Sumi, N. Moriwaki, G. Nakane, T. Nakakuma, Y. Judai, Y. Uemoto, Y. Nagano, S. Hayashi, M. Azuma, E. Fujii, S.I. Katsu, T. Otsuki, L. McMillan, C. Paz de Araujo, and G. Kano, "A 256 kb nonvolatile ferroelectric memory at 3 V and 100 ns," *Digest of Technological Paper - IEEE International Solid-State Circuits Conference*, pp. 268-269, Feb. 1994.

[5] S. S. Eaton, D. B. Butler, M. Parris, D. Wilson, and H. McNeillie, "A ferroelectric nonvolatile memory," *Digest of Technological Paper - IEEE International Solid-State Circuits Conference*, vol. 130, pp. 130-131, Feb. 1988.

[6] J. Evans and R. Womack, "An experimental 512-bit nonvolatile memory with ferroelectric storage cell," *IEEE Journal of Solid-State Circuits*, vol. 23, pp. 1171-1175, no. 5, Oct. 1988.

[7] R. Womack and D. Tolsch, "A 16 kb Ferroelectric nonvolatile memory with a bit parallel architecture," *Digest of Technological Paper - IEEE International Solid-State Circuits Conference*, vol. 351, pp. 242-243, Feb. 1989.

[8] T. Hayashi, Y. Igarashi, D. Inomata, T. Ichimori, T. Mitsuhashi, K. Ashikaga, T. Ito, M. Yoshimaru, M. Nagata, S. Mitarai, H. Godaiin, T. Nagahama, C. Isobe, H. Moriya, M. Shoji, Y. Ito, H. Kuroda, and M. Sasaki, "A novel stack capacitor cell for high density FeRAM compatible with CMOS logic," *Technology Digest - IEEE International Electron Devices Meet.*, pp. 543-546, Dec. 2002.

[9] H. McAdams, R. Acklin, T. Blake, D. Xiao-Hong, J. Eliason, J. Fong, W.F. Kraus, D. Liu, S. Madan, T. Moise, S. Natarajan, Ning Qian, Yunchen Qiu, K.A. Remack, K.A. J. Rodriguez, Roscher, A. Seshadri, and S.R. Summerfelt, "A 64-Mb embedded FRAM utilizing a 130-nm 5LM Cu/FSG logic process," *IEEE Journal of Solid-State Circuits*, vol. 39, no. 1, pp. 667-677, Apr. 2004.

[10] T.S.Moise, S. R. Summerfelt, H. McAdams, S. Aggarwal, K.R. Udayakumar, F.G. Celii, J.S. Martin, G. Xing, L. Hall, K.J. Taylor, T.Hurd, J. Rodriguez, K. Remack, M.D. Khan, K. Boku, G. Stacey, M. Yao, M.G.Albrecht, E. Zielinski, M. Thakre, S. Kuchimanchi, A. Thomas, B. McKee, J. Rickes, A. Wang, J. Grace, J. Fong, D. Lee, C. Pietrzyk, R. Lanham, S.R. Gilbert, D. Taylor, J. Amano, R. Bailey, F. Chu, G. Fox, S. Sun, and T. Davenport, "Demonstration of a 4 Mb, high density ferroelectric memory embedded within a 130 nm, 5 LM Cu/FSG logic process," *Technology Digest - IEEE International Electron Devices Meet.*, pp. 535-538, Dec. 2002.

[11] K. Sugibuchi, Y. Kurogi, and N. Endo, "ferroelectric field-effect memory device using $Bi_4Ti_3O_{12}$ film," *Journal of Applied Physics*, vol. 46, no. 7, pp 2877-2881, Jul. 1975.

[12] A. Kingon, P. Muralt, N. Setter, and R. Waser, "Ceramic materials for electronics," edited by R. E. Buchanan (Dekker, New York), pp. 465-526, 2004.

[13] H. T. Lue, C. J. Wu, and T. Y. Tseng, "Device modeling of ferroelectric memory field-effect transistor for the application of ferroelectric random access memory," *Ultrasonics, Ferroelectrics and Frequency Control*, vol. 5, no. 1, pp. 5-14, Jan. 2003.

[14] S. L. Miller and P. J. McWhorter, "Physics of the ferroelectric nonvolatile memory field effect transistor," *Journal of Applied Physics*, vol. 72, no. 12, pp. 5999-6010, Dec. 1992.

[15] S. H. Lim, A. C. Rastogi, and S. B. Desu, "Electrical properties of metal-ferroelectric-insulator-semiconductor structures based on ferroelectric polyvinylidene fluoride copolymer film gate for nonvolatile random access memory application," *Journal of Applied Physics*, vol. 96, no. 10, pp. 5673-5682, Nov. 2004.

[16] I. M. Ross, "Semiconductive translating device," U.S. Patent, no. 2791760, 1957.

[17] J. L. Moll and Y. Tarui, "A new solid state memory resistor," *IEEE Transactions on Electron Devices*, ED-10, pp. 338, Sep. 1963.

[18] S. Y. Wu, "A new ferroelectric memory device, metal-ferroelectric-semiconductor transistor," *IEEE Transactions on Electron Devices*, ED-21, pp. 499-504, Aug. 1974.

[19] Y. Arimoto and H. Ishiwara, "Current status of ferroelectric random-access memory," *MRS Bulletin.*, vol. 29, no. 11, pp. 823-828, Nov. 2004.

[20] H. Ishiwara, *Material Research Society Symposium Proc.*, vol. 596, pp427, 2000.

[21] K. Takahashi, K. Manabe, A. Morioka, T.

Ikarashi, T. Yoshihara, H. Watanabe, and T. Tatsumi, *Abstracts of the International Conference Solid State Devices and Materials (Tokyo)(unpublished)* no. 1-2, 2004.

[22] H. Kohlstedt and H. Ishiwara, "In nanoelectronics and information technology: advanced electronic materrial and novel devices," edited by R. Waser (Wiley-VCH, Weinheim) , pp. 387, 2002.

[23] Q. M. Zhang, H. Xu, F. Fang, Z.-Y. Cheng, and F. Xia, "Critical Thickness of Crystallization and Discontinuous Change in Ferroelectric Behavior with Thickness in Ferroelectric Polymer Thin Films," *Journal of Applied Physics*, vol. 89, no. 5, pp. 2613-2616, Mar. 2001.

[24] F. Xia, H. Xu, F. Fang, B. Razavi, Z.-Y. Cheng, Y. Lu, B. Xu, and Q. M. Zhang, "Thickness dependence of ferroelectric polarization switching in poly(vinylidene fluoride–trifluoroethylene) spin cast films," *Applied Physics Letters*, vol. 78, no. 8, pp. 1122-1124, Feb. 2001.

[25] Q. Gao and J. I. Scheinbeim, "Dipolar intermolecular interactions, structural development, and electromechanical properties in ferroelectric polymer blends of nylon-11 and poly(vinylidene fluoride)," vol. 33, no. 20, pp. 7564-7572, Sep. 2000.

[26] Y. Tajitsu, K. Ishida, S. Kanbara, H. Ohigashi, M. Date, and E. Fukada, "Temperature dependence of switching characteristics in polyurea-5 thin films," *Japanese Journal of Applied Physics*, vol. 37, no. 9B, pp. 5375-5378, Sep. 1998.

[27] T. T. Wang, J. M. Herbert, and A. M. Glass, "The applications of ferroelectric polymers Glasgow," (Blackie, U.K.), 1988.

[28] H. S. Nalwa, "Ferroelectric polymer" (Marcel Dekker, New York) , pp. 895, 1995.

[29] A. J. Lovinger, "Poly(vinylidene fluoride) developments in crystalline polymers—I" (D. C. Basset, Ed. London, U.K.: Applied Sciences) , pp. 195-273, 1981.

[30] T. Furukawa, "Ferroelectric properties of vinylidene fluoride copolymers," *Phase Transit.*, vol. 18, no. 3-4, pp. 143-211, 1989.

[31] R. G. Kepler and R. A. Anderson, "Ferroelectric polymers," *Advanced in Physics*, vol. 41, no. 1, pp. 1-57, Jan./Feb. 1992.

[32] R. G. Kepler and R. A. Anderson, "Ferroelectricity in polyvinylidene fluoride," *Journal of Applied Physics*, vol. 49, no. 3, pp. 1232-1235, Mar. 1978.

[33] R. C. G. Naber, C. Tanase, P. W. M. Blom, G. H. Gelinck, A. W. Marsman, F. J. Touwslager, S. Setayesh, and D. M. de Leeuw, "High-performance solution-processed polymer ferroelectric field-effect transistors," *Nature Materials*, vol. 4, no. 3, pp. 243-248, Mar. 2005.

[34] A. J. Lovinger, "Ferroelectric transition in a copolymer of vinylidene fluoride and tetrafluoroethylene," *Macromolecules*, vol. 16, no. 9, pp. 1529-1534, Jan. 1983.

[35] K. Noda, K. Ishida, T. Horiuchi, K. Matsushige, and A. Kubono, "Structures of vinylidene fluoride oligomer thin films on alkali halide substrate," *Journal of Applied Physics*, vol. 86, no. 7, pp. 3688-3693, Oct. 1999.

[36] K. Noda, K. Ishida, A. Kubono, T. Horiuchi, H. Yamada, and K. Matsushige, "Structures and ferroelectric natures of epitaxially grown vinylidene fluoride oligomer thin films," *Japanese Journal of Applied Physics*, vol. 39, no. 11, pp. 6358-6363, Nov. 2000.

[37] A.C. Rastogi and S.B. Desu, "Ferroelectric poly(vinylidene fluoride) thin film grown by low-pressure chemical vapor polymerization," *Chemical Vapor Deposition*, vol. 12, pp. 742-750, Dec. 2006.

[38] A.V. Bune, V.M. Fridkin, S. Ducharme, L.M. Blinov, S.P. Palto, A.V. Sorokin, S.G. Uudin, and A. Zlatkin, "Two-dimensional ferroelectric films," *Nature*, vol. 391, pp. 874-877, Feb. 1998.

[39] F. Xia and Q. M. Zhang, "Schottky emission at the metal polymer interface and its effect on the polarization switching of ferroelectric poly (vinylidene fluoride-trifluoroethylene) copolymer thin films," *Applied Physics Letters*, vol. 85, no. 10, pp. 299-306, Sep. 2004.

[40] G. Zhu, Z. Zeng, L. Zhang, and X. Yan, "Polarization fatigue in ferroelectric vinylidene fluoride and trifluoroethylene copolymer films," *Applied Physics Letters*, vol. 89, pp. 102905-1-10292905-3, Sep. 2006.

[41] Y. J. Park, S. J. Kang, C. Park, K. J. Kim, H. S. Lee, M. S. Lee, U. Chung, and I. J. Park, "Irreversible extinction of ferroelectric polarization

in P(VDF-TrFE) thin films upon melting and recrystallization," *Applied Physics Letters*, vol. 88, pp. 242908-1-242908-3, Sep. 2006.

[42] H. Xu, J. Zhong, X. Liu, J. Chen, and D. Shen, "Ferroelectric and switching behavior of poly (vinylidene fluoride-trifluoroethylene) copolymer ultrathin films with polypyrrole interface," *Applied Physics Letters*, vol. 90, pp. 092903-1-092903-3, Mar. 2007.

[43] Y. J. Park, S. J. Kang, C. Park, E. Woo, K. Shin, and K. J. Kim, "Recovery of remanent polarization of poly(vinylidene fluoride-trifluoroethylene) thin film after high temperature annealing using topographically nanostructured aluminium bottom electrode," *Applied Physics Letters*, vol. 90, pp. 222903-1-222903-3, May 2007.

[44] Y. J. Park, S. J. Kang, C. Park, B. Lotz, A. Thierry, K. J. Kim, and J. Huh, "molecular and crystalline microstructure of ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) ultrathin films on bare and self-assembled monolayer-modified Au Substrates," *Macromolecules*, vol. 41, no. 1, pp. 109 - 119, Oct. 2008.

[45] T. J. Reece, S. Ducharme, A. V. Sorokin, and M. Poulsen, "Nonvolatile memory element based on a ferroelectric polymer Langmuir–Blodgett film," *Applied Physics Letters*, vol. 82, no. 1, pp. 142-144, Jan. 2003.

[46] S. Fujisaki, H. Ishiwara, and Y. Fujisaki, "Low-voltage operation of ferroelectric poly(vinylidene fluoride-trifluoroethylene) copolymer capacitors and metal-ferroelectric- insulator-semiconductor diodes," *Applied Physics Letters*, vol. 90, pp. 162902-1 - 162902-3, Apr. 2007.

[47] R. Schroeder, L. A. Majewski, and M. Grell, "All-organic permanent memory transistor using an amorphous, spin-cast ferroelecric-like gate insulator," *Advanced Materials*, vol. 16, no. 7, pp. 633-636, Apr. 2004.

[48] K. N. N. Unni, R. de Bettignies, S. Dabos-Seignon, and J. Nunzi, "A nonvolatile memory element based on an organic field-effect transistor," *Applied Physics Letters*, vol. 85, no. 10, pp. 1823 - 1825, Sep. 2004.

[49] Y. Matsuo, T. Ijicji, H. Yamada, J. Hatori, and S. Ikehata, "Electrical properties and memory effect in the field effect transistor based on organic ferroelectric insulator and pentacene," *Central Eurpean Journal of Physics*, vol. 2, no.2, pp. 357-366, Jan. 2004.

[50] R. C. G. Naber, C. Tanase, P. W. M. Blom, G. H. Gelinck, A. W. Marsman, F. J. Touwslager, S. Setayesh, and D. M. D. Leeuw, "High-performance solution-processed polymer ferroelectric field-effect transistor," *Nature Materials*, vol. 4, pp.243 - 2005, Feb. 2005.

[51] R. C. G. Naber, P. W. M. Blom, A.W. Marsman, and D. M. de Leeuw, "Low voltage switching of a spin cast ferroelectric polymer," *Applied Physics Letters*, vol. 85, pp. 2032-2034, Jul. 2004.

[52] F. A. Yildirim, C. Ucurum, R. R. Schliewe, R. M. Meixner, H. Goebel, and W. Krautschneider, "Spin-cast composite gate insulation for low driving voltages and memory effect in organic field-effect transistors," *Applied Physics Letters*, vol. 90, pp. 083501-1-083501-3, Feb. 2007.

[53] S. H. Noh, W. Choi, M. S. Oh, D. K. Hwang, K. Lee, S. Im, S. Jang, and E. Kim, "ZnO-based nonvolatile memory thin-film transistors with polymer dielectric/ferroelectric double gate insulators," *Applied Physics Letters*, vol. 90, pp. 253504-1-253504-3, Jun. 2007.

[54] S. J. Kang, Y. J. Park, J. Sung, P. S. Jo, C. Park, K. J. Kim, and B. O. Cho, "Spin cast ferroelecric beta poly(vinylidene fluoride) thin films via rapid thermal annealing," *Applied Physics Letters*, vol. 92, pp. 012921-1-012921-1, Jan. 2008.

[55] Wang, J. Li, H. Liu, J. Duan, Y. Jiang, and S. Yan, "On the $\alpha \rightarrow \beta$ transition of carbon-coated highly oriented PVDF ultrathin film induced by melt recrystallization," *Journal of the American Chemical Society*, vol. 125, no. 6, pp.1496-1497.

[56] S. J. Kang, Y. J. Park, J. Hwang, H. J. Jeong, J. S. Lee, K. J. Kim, H. Kim, J. Huh, and C. Park, "Localized pressure-induced ferroelectric pattern arrays of semicrystalline poly(vinylidene fluoride) by microimprinting," *Advanced Materials*, vol. 19, no. 4, pp. 581-586, Feb. 2007.

[57] Z. Hu, G. Baralia, V. Bayot, J.-F. Gohy, and A. M. Jonas, "Nanoscale control of polymer crystallization by nanoimprint lithography," *Nano Letters*, vol. 5, no. 9, pp. 1738-1743, Jul. 2005.

[58] Y. J. Park, Y. S. Kang, and C. Park, "Micropatterning of semicrystalline poly(vinylidene fluoride) (PVDF) solutions," *European Polymer Journal*, vol. 41, pp. 1002-1012, Jan. 2005.

[59] L. Zhang, S. Ducharme, and J. Li, "Microimprinting and ferroelectric properties of poly(vinylidene fluoride-trifluoroethylene) copolymer films," *Applied Physics Letters*, vol. 91, pp. 172906-1-172906-3, Oct. 2007.

[60] K. Kimura, K. Kobayashi, H. Yamada, and K. Matsushige, "investigation of molecular chain orientation change of polymer crystals in phase transitions by friction anisotropy measurement," *Langmuir*, vol. 23, no. 9, pp. 4740-4745, Feb. 2007.

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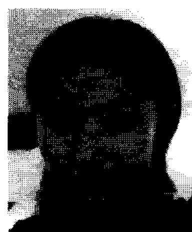

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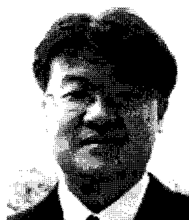

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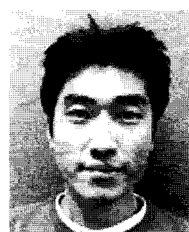

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