Review Article
Ferroelectric Polymer Thin Films for Organic Electronics

Manfang Mai,[1,2] Shanming Ke,[1] Peng Lin,[1] and Xierong Zeng[1,2]

[1]*College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China*
[2]*Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province,*
 College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

Correspondence should be addressed to Shanming Ke; smke@szu.edu.cn and Xierong Zeng; zengxier@szu.edu.cn

The considerable investigations of ferroelectric polymer thin films have explored new functional devices for flexible electronics industry. Polyvinylidene fluoride (PVDF) and its copolymer with trifluoroethylene (TrFE) are the most commonly used polymer ferroelectric due to their well-defined ferroelectric properties and ease of fabrication into thin films. In this study, we review the recent advances of thin ferroelectric polymer films for organic electronic applications. Initially the properties of ferroelectric polymer and fabrication methods of thin films are briefly described. Then the theoretical polarization switching models for ferroelectric polymer films are summarized and the switching mechanisms are discussed. Lastly the emerging ferroelectric devices based on P(VDF-TrFE) films are addressed. Conclusions are drawn regarding future work on materials and devices.

1. Introduction

In recent years, driven by the rapidly developing miniaturized electronics, new organic devices based on polyvinylidene fluoride (PVDF) and its copolymer with trifluoroethylene (TrFE) thin films have attracted intensive research interest. Generally, ferroelectrics exhibit a striking finite size effect [1]. The switching time and the coercive field increase with decreasing film thickness while reversely the remanent polarization and the phase transition temperature decrease with decreasing thickness. For applications which require low-voltage operation such as nonvolatile memories, the ferroelectric films should be thin enough for low operation voltage at the same time they should have sufficient and stable ferroelectric properties to maintain the memory functionality.

PVDF and its copolymer with TrFE are the representative and the most important organic ferroelectric materials. The ferroelectricity in PVDF and P(VDF-TrFE) originates from molecular dipoles associated with electropositive hydrogen atoms and electronegative fluoride atoms, which are switchable upon an external field [2]. They are promising candidates for the next generation nonvolatile high-density memory applications which can replace perovskite ceramics currently used in the commercial ferroelectric random access memories (FRAMs) [3–5]. Their attractive advantages include low temperature processing, low-cost solution processing, outstanding chemical stability, and nontoxicity [6]. In the past few years, there have been considerable research activities to combine P(VDF-TrFE) films as nonvolatile memory cells such as metal-ferroelectric-insulator-semiconductor (MFIS) diode [7–11] and ferroelectric-field-effect-transistor (FeFET) [12–15]. The key issues for optimizing the memory performance including switching time, switching voltage, retention, and endurance still need to be overcome. Recently, PVDF and its copolymer find their new way for the emerging applications in organic electronics, such as negative capacitance devices [16], organic photovoltaic cells [17], and multiferroic tunnel junctions [18].

The discovery of Langmuir-Blodgett (LB) ferroelectric polymer films in 1995 [19] led to investigation of ferroelectric properties at the nanoscale. For P(VDF-TrFE) films, the ferroelectricity and polarization switching have been found for two monolayers (l = 1 nm) [20]. It opened the way for investigation of finite size effect at the nanoscale. Since then, it has been a subject of intensive study not only in theoretical aspects but also in technical applications. The results on
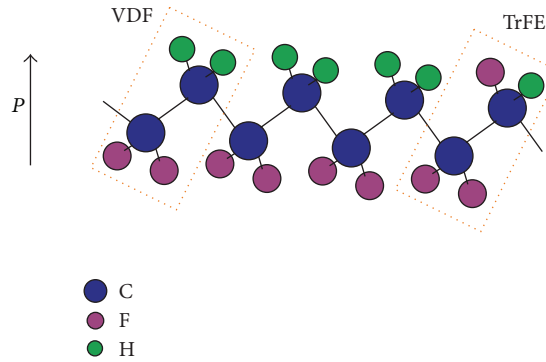
FIGURE 1: Schematic of molecular structure of P(VDF-TrFE) in the β phase. The polarization direction points from fluoride to hydrogen atoms.

P(VDF-TrFE) LB films provide many new insights into the fundamental physics: the existence of two-dimensional ferro-electrics with nearly absence of finite size effects on the bulk transition (a first order phase transition with a transition temperature nearly equal to the bulk value) [20], the transition from extrinsic (switching with nucleation and domain wall motion) to intrinsic (switching without domain) ferroelectric switching in the context of Landau-Ginzburg mean-field theory below a thickness of 15 nm [21], and so forth. However, there have been strong debates of the theoretical models used to explain the experiments. Scott pointed out that the presence of two apparent phase transition temperatures interpreted as true two-dimensional surface ferroelectricity by the Moscow-Nebraska group, instead, can be explained by the seminal Tilly-Zeks theory and its extension by Duiker to first order phase transition [22]. Several groups spoke against the intrinsic nature of the switching as the experiments lack several key features of intrinsic switching [23–27]. Lately, the Moscow-Nebraska group demonstrated some new experiment evidences to support their claim of domain-free Landau switching in P(VDF-TrFE) LB films [28, 29] as well as in ultrathin BaTiO$_3$ films [30], suggesting that homogeneous switching in ultrathin films is a common phenomenon for all ferroelectric materials. Currently, the explanations for the switching behavior in P(VDF-TrFE) thin films are still controversial.

PVDF is a rich system for both practical applications and academic investigations including phase transition and switching mechanism. The main objective of this paper is to review the current research status of ferroelectric polymer films with emphases on switching mechanism and ferro-electric devices based on P(VDF-TrFE) films particularly with the thickness below one hundred nanometers. The development of ferroelectric polymer thin film devices will have a significant impact on organic electronics.

2. Ferroelectric Polymers

The piezoelectricity in poled PVDF was discovered in 1969 [31] followed by the discovery of the pyroelectricity in PVDF in 1971 [32]. However, it was not until the late 1970s that the ferroelectricity in PVDF was confirmed [33, 34].

The distinguishing characteristics of PVDF and its copoly-mers include highly compact structure, high chemical sta-bility, large permanent dipole moment, ease of fabrication, and low annealing temperature which can be integrated with other materials and processes, for example, silicon microfabrication.

PVDF exhibit four polymorphic crystalline forms: α, β, γ, and δ phases, whose formations depend on crystallization conditions, electrical poling, and mechanical drawing. The β phase has an orthorhombic structure with an all-trans (TTTT) molecule conformation possessing a large sponta-neous polarization and is responsible for the ferroelectric and piezoelectric properties. The dipoles in the β-PVDF extend from the electronegative fluoride atoms to the slightly electropositive hydrogen atoms perpendicular to the polymer chain direction, producing a dipole moment of 7×10^{-30} C·m (2 Debyes), as shown in Figure 1. Recently δ-PVDF is success-fully fabricated as an overlooked polymorph of PVDF pro-posed 30 years ago [35]. The remanent polarization and coercive field are comparable to those of β-PVDF and of P(VDF-TrFE) while the thermal stability is enhanced due to its higher Curie temperature.

The introduction of TrFE, which has three fluoride atoms per monomer, to copolymerize with PVDF, can enhance the all-trans conformation associated with the β phase. This is because the fluoride atom is larger than hydrogen atom and therefore it can induce a stronger steric hindrance [2]. In addition, the copolymer with TrFE can be annealed to much higher crystallinity than pure PVDF [36]. The most studied copolymers have a composition of P(VDF-TrFE 70/30), which has a maximum spontaneous polarization around 10 μC/cm^2 [37]. Another feature for the introduction of TrFE is that it can lower the phase transition temperature T_c in the copolymers. P(VDF-TrFE) with molar ratios of 50–80% of PVDF undergoes a clear ferroelectric-paraelectric phase transition with a measurable Curie point. The T_c increases with increasing PVDF content from 70°C at 50 mol% to 140°C at 80 mol%. The transition is an order-disorder type while the disorder is a random mixture of trans- and gauche combinations in the conformation of the molecules. More-over, the transition tends to change from a first order to

a second order as the PVDF content decreases to a 52/48 composition with evidence of the disappearance of thermal hysteresis [38]. In the bulk PVDF the phase transition is not accessible with experiments because the melting temperature of this ferroelectric polymer (~170°C) is lower than the point of the possible phase transition T_c. Until very recently, a first order ferroelectric phase transition in the Langmuir-Blodgett ultrathin PVDF films was observed for the first time [39]. We have found the thickness interval where ferroelectric phase transition disappears and transition from ferroelectric to pyroelectric state takes place in PVDF Langmuir-Blodgett films and explain the shift of T_c by the finite size effect at the nanoscale using Landau-Ginzburg-Devonshire theory and the Weiss mean field model [40].

3. Thin Films Fabrication

3.1. Spin Coating. Conventionally, ferroelectric thin films are prepared by solvent spinning method which is very attractive for researchers due to its ease of processing and good quality of film surface. PVDF and its copolymers can be dissolved in a variety of organic solvents for spin coating, such as 2-butanone, dimethylsulfoxide (DMSO), dimethylformamide (DMF), and methylethylketone (MEK). The sample thickness can be controlled by varying the solution concentrations and rotating speeds. P(VDF-TrFE) films prepared by spin coating consist of both crystalline and noncrystalline regions [2]. Uniform and compact ferroelectric films thinner than 60 nm are usually difficult to achieve by spin coating. Lately, with the improvement of experimental conditions, some groups can produce ferroelectric copolymer films even down to 10 nm by spin coating [35, 44, 45]. Li et al. [46] reported that homogeneous and smooth thin PVDF films can be prepared either at low relative humidity or at high substrate temperature. Figure 2 shows the surface morphology evolution of PVDF thin films as a function of both relative humidity and substrate temperature. At high relative humidity the film surface is porous and loose. With decreasing humidity, the film becomes homogeneous and dense (Figure 2(a)). On the other hand (Figure 2(b)), fixing the relative humidity at 25% the surface morphology of PVDF films is denser and smoother as the substrate temperature is increased from 20°C to 100°C. The microstructure of PVDF thin films is determined by the phase separation mechanism.

3.2. Langmuir-Blodgett Technique. Two-dimensional ferroelectric polymer films can be fabricated by Langmuir-Blodgett (LB) technique which allows precise control of film thickness down to one monolayer with high crystallinity. The principle of LB technique is the amphiphilic property of molecules which are composed of a hydrophilic part and a hydrophobic part [47]. Amphiphilic molecules are trapped at the interface with one type of bonding being attracted to polar media such as water and the other type of bonding being much less water soluble. The LB films are achieved through subsequent transfer of monolayers from gas-liquid interface onto a solid substrate. The transfer can be done by either vertical or horizontal dipping with the latter called horizontal Langmuir-Schaefer method, as shown in Figure 3(a) [37].

Although P(VDF-TrFE) copolymer is not amphiphilic, the large molecular weight of polymers with low solubility in water can be dispersed to form a sufficiently stable layer on water with a repeatable pressure area isotherm (Figure 3(b)), which identifies the conditions forming closest packing of a film of monolayer thickness [37]. Good quality P(VDF-TrFE 70/30) LB films are deposited from a copolymer solution in dimethylsulfoxide (DMSO) with concentration of 0.01 wt.% and target pressure of 3 mN/m [48, 49].

Generally, the as-prepared films need to be annealed close to the crystallization temperature to increase the crystallinity. It is reported that the thermal annealing increases the film surface roughness [46]. Alternately, smooth PVDF thin films can be prepared using elevated substrate temperatures and applying a short electrical pulse [35]. Different materials have served as electrodes for P(VDF-TrFE) films including aluminum [20, 50, 51], platinum [52, 53], gold [44, 54, 55], silver [54, 56], copper [52], nickel [52], indium [45], sodium [57], and conducting PEDOT/PSS copolymer [58]. The most commonly used electrode is aluminum. The advantages of aluminum electrode are its low deposition temperature, chemical passivation, and suppressing of charge injection from the metal electrode. However, the formation of the oxide layer (Al_2O_3) between the electrode and the ferroelectric film inhibits fast switching of the films.

4. Polarization Switching Mechanism

The switching behavior of ferroelectric polymer thin films has been extensively investigated to understand the kinetics of polarization switching, which is very critical for intentional design and preparation of materials for various purposes. Domain nucleation and domain wall motion mechanism for polarization reversal was established early by Merz [59] and Little [60] and later by Miller [61, 62] and Fatuzzo [63]. The studied ferroelectric material was barium titanate ($BaTiO_3$). Numerous models have been proposed to quantify domain phenomena and their effects on ferroelectric switching. The classical model to describe ferroelectric switching kinetics is the Kolmogorov-Avrami-Ishibashi (KAI) model [1, 64, 65], which is based on the study of statistical behavior and the probability of nucleation and growth of domains. An alternative model is the nucleation-limited switching (NLS) model for thin films developed by Tagantsev et al. [66, 67]. For P(VDF-TrFE) ultrathin films, ferroelectric switching may not include the usual nucleation and domain propagation processes. Here, the existing theoretical models for ferroelectric switching are summarized.

4.1. Kolmogorov-Avrami-Ishibashi (KAI) Model. Polarization reversal in ferroelectrics proceeds by the nucleation of reversed nuclei followed by the forward and sideways growth of the reversed areas, as shown in Figure 4 [63]. When a field is applied with the opposite polarity, small nuclei of domain with reverse polarization direction appear, usually at the interfaces or grain boundaries (Figure 4(a)). Each nucleus grows parallel or antiparallel to the applied field until it becomes a domain and reaches the opposite side (Figure 4(b)). The domain formed in this way starts expanding

20°C

Top view   Cross section

60%

40%

25%

5%

0%

10μm   2μm

(a)

25% humidity

Top view   Cross section

20°C

40°C

50°C

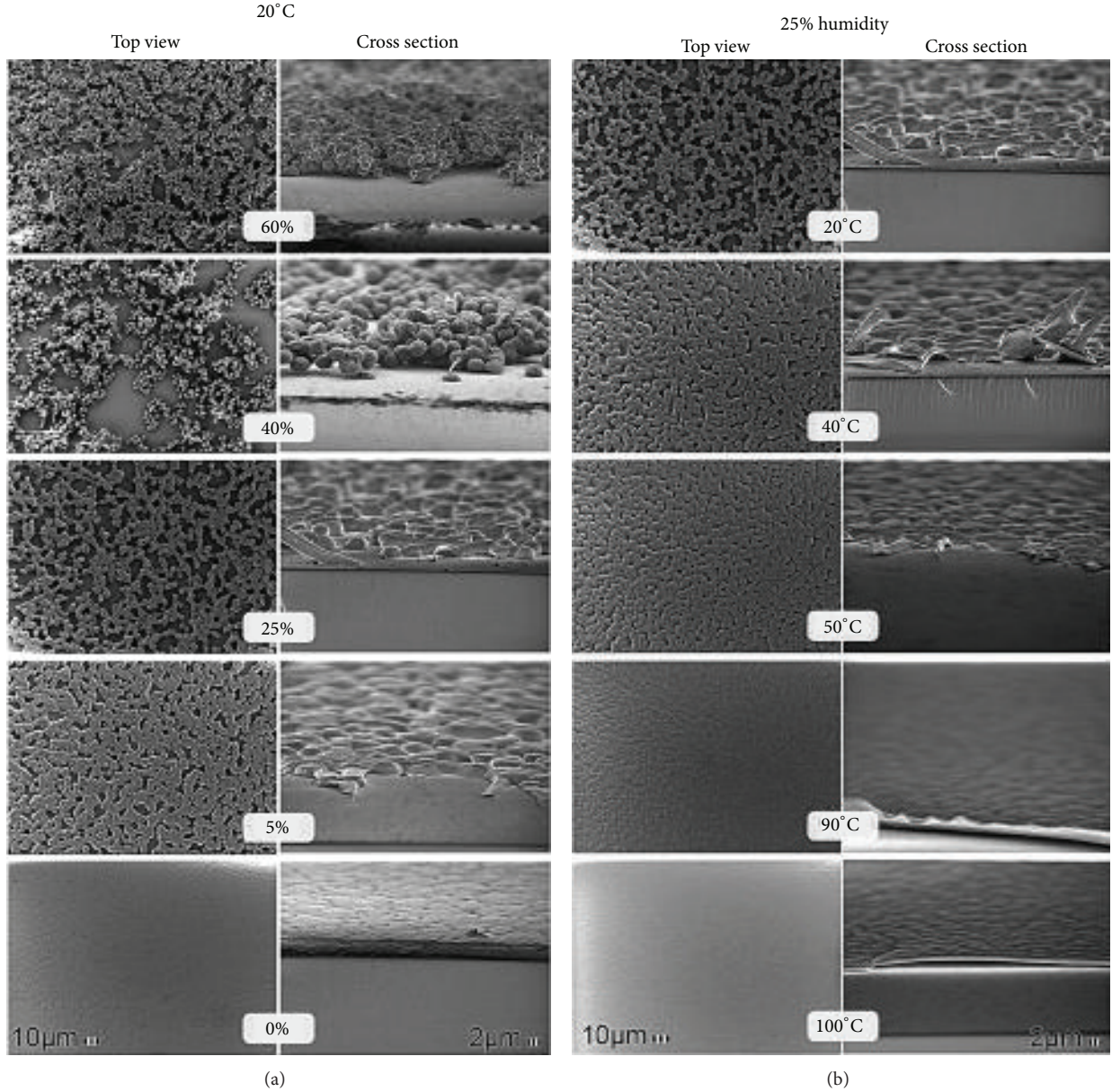90°C

100°C

10μm   2μm

(b)

Figure 2: Surface morphology evolution of PVDF thin films. (a) Top view and cross section SEM micrographs of PVDF thin films presented as a function of the relative humidity between 0% and 60%. The films were deposited at room temperature, 20°C. The scale bars of 10 μm and 2 μm are presented in the bottom micrographs. (b) Top view and cross section SEM micrographs of PVDF thin films presented as a function of the deposition temperature between 20°C and 100°C. The relative humidity was fixed at 25% [46].

sideways (Figure 4(c)). After some time these domains are large enough to join each other and become coalescence (Figure 4(d)). The above successive processes will repeat until the polarization is completely reversed in the whole sample.

The Kolmogorov-Avrami-Ishibashi (KAI) model is applicable and very useful for analyzing the above switching process in many materials including single crystals [66, 68] as well as epitaxial thin film ferroelectrics [69]. In the scope of KAI model, the ferroelectric media where the polarization reversal takes place are infinite. The reversed polarization $P(t)$ and the switching current $I(t)$ can be written as

$$P(t) = 2P_s \left\{ 1 - \exp\left[-\left(\frac{t}{t_0} \right)^n \right] \right\}, \qquad (1)$$

$$I(t) = 2P_s S_0 \frac{n}{t_0} \left(\frac{t}{t_0} \right)^{n-1} \exp\left[-\left(\frac{t}{t_0} \right)^n \right], \qquad (2)$$

where P_s is spontaneous polarization, S_0 is electrode area, t_0 is switching time, and n can be an integer (α-model or β-model) or non-integer value (mixture of α-model and β-model) between 1 and 3 depending on the dimension of the system. A plot of the switching current profiles for different values of n according to (2) is depicted in Figure 5. The tick labels in the axes would be different for a variation of parameters P_s, S_0, and t_0 in different samples. Figure 5 shows qualitatively different shapes of the switching currents. For $n > 1$, there is a peak in the current transients. For $n \leq 1$, it is not possible to identify a current maximum. However, there is no physical
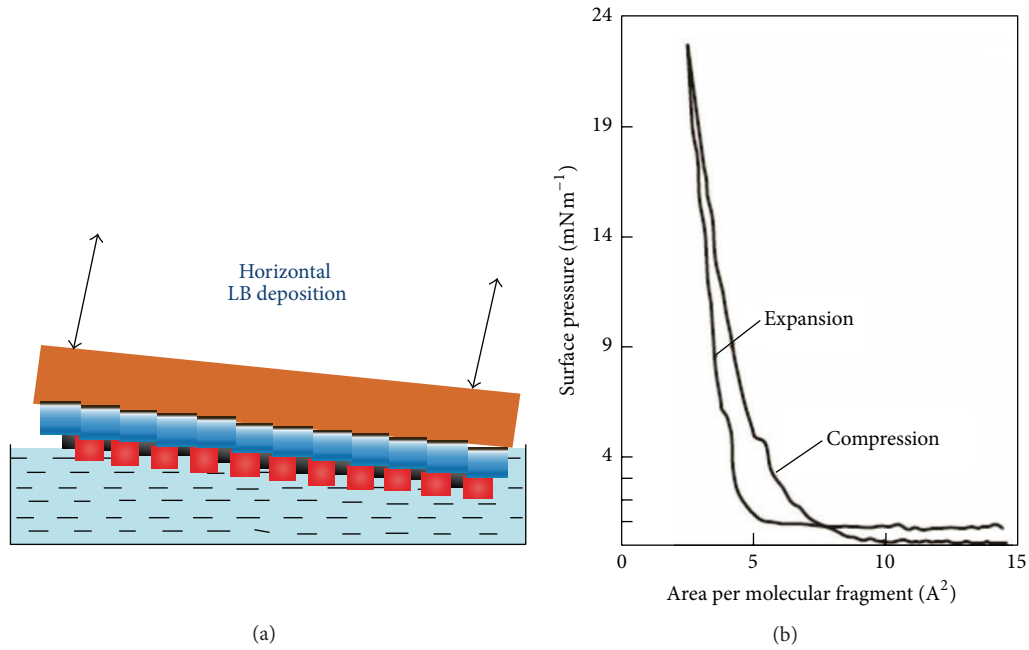
FIGURE 3: (a) Diagram of the Langmuir-Schaefer monolayer deposition method. (b) Pressure-area isotherm of P(VDF-TrFE 70/30) [37].
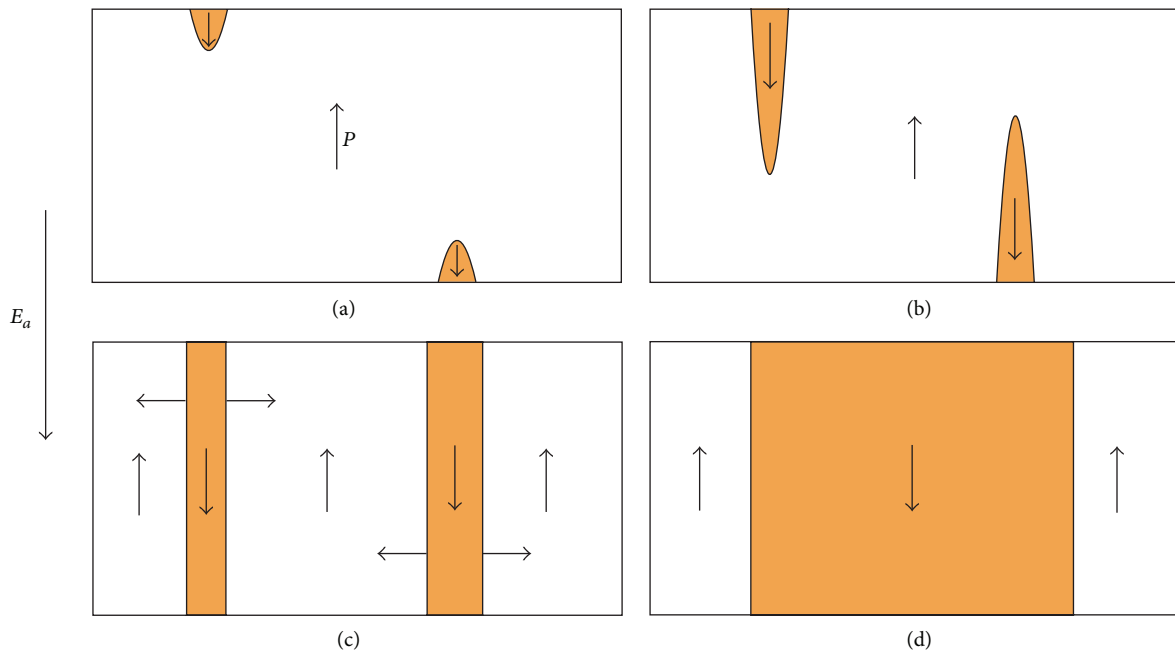

FIGURE 4: The evolution of the domain structure in ferroelectric during switching under an application of electric field (a) nucleation of new domains, (b) forward growth, (c) sideways expansion, and (d) coalescence, after [63].

meaning in the framework of KAI model for an n value less than 1 since the growth dimensionality could never be less than 1. Therefore a current maximum should always exist in the switching transient when the sample is suppressed by a field above the coercive field in the framework of KAI model. Moreover, KAI model describes a thermally activated switching.

The KAI model assumes unrestricted domain growth in an infinite media. Due to the simplified assumptions, it encounters problems when it comes to precisely describe the switching behavior in real finite ferroelectrics especially for polycrystalline films and ceramics. Therefore, later on new models are constructed to give a more realistic and appropriate description of polarization reversal.

4.2. Nucleation-Limited Switching (NLS) Model. Tagantsev et al. [67] developed an alternative scenario of a nucleation-limited switching (NLS) model which is successful to describe
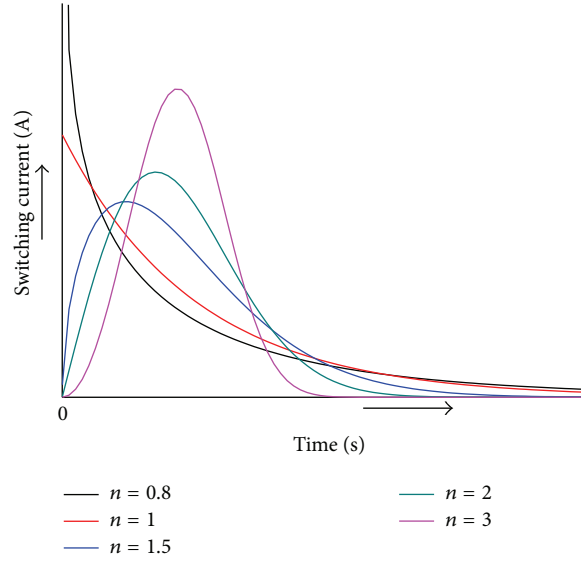
FIGURE 5: Switching current profiles for n with different values according to (2).

the switching kinetics in $Pb(Zr,Ti)O_3$ thin films. This model assumes that the film consists of many areas, which switch independently. The switching in an area is considered to be triggered by an act of the reverse domain nucleation. They used a distribution function of the switching times to describe the ensemble of the elementary regions. In the framework of the NLS model, the nucleation time is assumed to be much longer than the time of domain wall motion and a distribution of switching time is modified in the expression of the time dependence of polarization, written as [67]

$$P(t) = 2P_s \int_{-\infty}^{\infty} \left\{ 1 - \exp\left[-\left(\frac{t}{t_0} \right)^n \right] \right\} F(\log t_0) \, d(\log t_0),$$
(3)

where $F(\log t_0)$ is the distribution function for $\log t_0$. It meets the normalizing condition:

$$\int_{-\infty}^{\infty} F(\log t_0) \, d(\log t_0) = 1.$$
(4)

The value of n is assumed to be 2 for thin film ferroelectrics and 3 for bulk ferroelectrics [67]. The switching dynamic extended in a wide time range can be described in terms of this model with a simple shape of the spectrum $F(\log t_0)$. Jo et al. [70] suggested to use the Lorentzian distribution of $\log t_0$, which can account for variations in the local electrical field related to the randomly distributed dipole defects. A Gaussian distribution can also be well adjusted to the random electric field distribution suggested by Zhukov et al. [71]. Mao et al. used the NLS model based on region-by-region switching to explain the switching kinetics of P(VDF-TrFE) thin films, which is successful to describe the polarization reversal behavior in the time domain for samples as thick as 100 nm [72].

Both KAI model and NLS model neglect the size of nuclei and domains. Fatuzzo [63] reported that the switching current maximum in time could be as broad as that of

a single relaxation process regardless of the domain growth dimensions, if the size of nuclei is taken into consideration. Numerical simulations in small systems using a local field method combined with dynamic Monte Carlo steps result in a monotonic decrease in the switching current [73].

4.3. The Weiss Mean Field Model. One hundred years ago Weiss [74, 75] proposed a model to describe phase transition in ferromagnetic materials. This model is actually a positive feedback model. The magnetic dipoles mutually evoke a field at the location of other dipoles which results in an alignment of all dipoles into the same direction. This local field which is also called Weiss field is only defined at the location of the dipoles. This model for magnetism was later applied to ferroelectrics [76].

In dielectrics Lorentz [77] developed a similar local field model. The local field at induced point dipoles for an infinite cubic lattice can be expressed as

$$E_{loc} = E_a + \frac{P}{3\varepsilon_0},$$
(5)

with E_a being the applied field and P the polarization of the matter. Equation (5) illustrates that the local field vice versa produces the dipole moments at the lattice points. It is the superposition of the applied field and the dipolar field which is proportional to the polarization itself. There are two types of dipoles: permanent dipoles fluctuating thermally activated in double well potentials and induced dipoles. The interaction between all these dipoles is considered with mean fields averaged over all particular local fields. The double well potentials, as shown in Figure 6, are characterized by their activation energy φ_0 and the distance between the wells l [78]. When no local field is present, the double wells are symmetrical and the dipoles are equally occupied in both directions. The net polarization of the whole system is zero. With a local field E_{loc} acting at the permanent dipoles the occupation changes and a net polarization results.
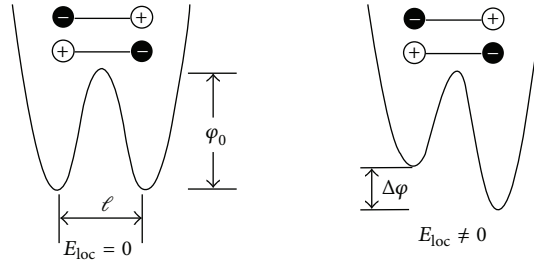
FIGURE 6: Permanent dipoles are assumed to fluctuate thermally activated in double well potentials. A local field shifts one well against the other redistributing the dipoles [78].

If only permanent dipoles are present, the local field within the Weiss model is assumed to be similar to (5):

$$E_{loc} = E_a + \alpha P, \tag{6}$$

where P is the macroscopic polarization which can be spontaneous below T_c or paraelectric above T_c. α is a coupling factor describing the strength of the interaction between the dipoles. The model is a mean field approach. It also contains microscopic elements including the properties of the double wells with the magnitude of the fluctuating dipole moments, the dipole densities, and the coupling constant α. Therefore the model can be considered as a link between phenomenological descriptions and molecular modeling [78].

With the Weiss model, several ferroelectric properties can be described, that is, ferroelectric hysteresis loop, the temperature dependence of the coercive field, the Curie-Weiss law for the electrical susceptibility, the buttery curves of the susceptibility in an external field, and a second order ferroelectric to paraelectric transition with its typical protraction in an applied electric field [78–80]. It has been shown that if additionally a strain in the material caused by the piezoelectric effect, that is, by the polarization itself, is taken into account, a second order phase transition changes to a first order [81]. In addition, the appearance of a double hysteresis close to the Curie temperature can be explained [82, 83].

Lately, Kliem and Kuehn [84] presented an analytical approach using the Weiss molecular mean-field model combined with the fluctuation of dipoles in double-well potentials to simulate the switching process with a maximum in the switching current as observed by Merz. The time-dependent switching process and the static polarization hysteresis loop are simulated which are in good qualitative agreement with experiments using the material parameters of P(VDF-TrFE). This theory is exact in the limit of infinite dimensions with homogeneous state and single domain.

4.4. The Homogenous Non-Domain Switching.

Recent studies using P(VDF-TrFE) copolymer Langmuir-Blodgett ultrathin films suggested that the switching kinetics in these films is different from the rules of nucleation and domain wall motion (extrinsic switching). This type of switching is called intrinsic switching which is defined by the absence of nucleation center and domain. The distinction between domain nucleated and continuous intrinsic switching mechanisms

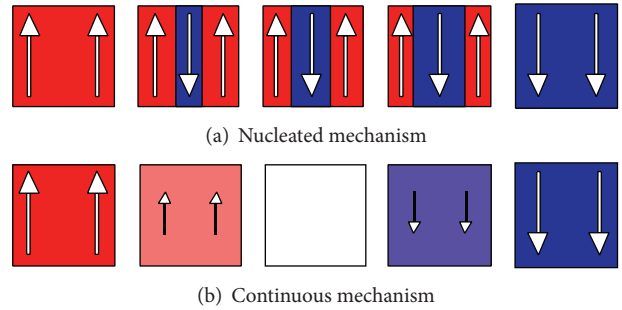(a) Nucleated mechanism

(b) Continuous mechanism

FIGURE 7: Schematic of polarization evolution during switching in a uniaxial ferroelectric. (a) Discontinuous nucleation and growth of inverted domains. (b) Continuous, uniform decrease of the polarization magnitude through zero without domain formation. Arrows indicate the orientation and magnitude of polarization [85].

can be illustrated in Figure 7 [85]. For intrinsic switching, it has a threshold field the intrinsic coercive field which is as high as 10^9 V/m. The polarization switching exhibits a critical behavior characterized by a pronounced slowing just above the threshold field [86]. In 2000 Ducharme et al. [21] reported that the intrinsic coercive field predicted by the Landau-Ginzburg theory of ferroelectricity was observed in P(VDF-TrFE) LB films below a thickness of 15 nm for the first time. They found that with decreasing thickness the coercive field first increases and then saturates for samples thinner than 15 nm, to a value of 5 MV/cm, which is in good agreement with the theoretical intrinsic value.

In intrinsic switching, the dipoles in the systems are highly correlated and tend to switch coherently or not at all. It can be described by Landau-Khalatnikov equations in the context of mean-field theory:

$$\xi \frac{dP}{dt} = -\frac{\partial G}{\partial P}, \tag{7}$$

$$G = \alpha (T - T_0) P^2 + \beta P^4 + \gamma P^6 - EP, \tag{8}$$

where P, G, E, and T are the polarization, the free energy, the electric field, and the temperature, respectively. ξ is a damping coefficient and T_0 is the Curie-Weiss temperature. α, β, and γ are constants assumed to be independent of temperature. By minimizing the free energy G in (8), a steady state hysteresis loop $P(E)$ can be derived, as shown in Figure 8 [86]. The solid lines in Figure 8(a) denote stable (AB and A′B′) or metastable
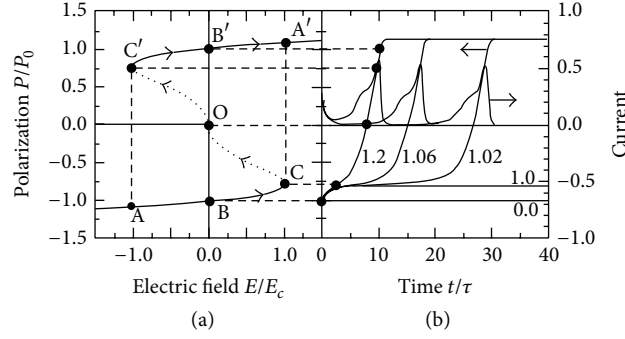
FIGURE 8: (a) The theoretical hysteresis loop $P(E)$ calculated from (7) and (8) for $T \approx T_0$. The solid lines represent stable or metastable states and the dotted line denotes unstable states. (b) Time evolution of the normalized polarization and current during switching at $T = T_0$ for several values of the normalized electric field. The horizontal dashed lines connect corresponding points in (a) to states in (b) [86].

(BC and B′C′) minima in the free energy. The dotted line (COC′) denotes unstable minima. Starting from a stable state B, if an opposite electric field which has an amplitude lower than the coercive field is applied, the polarization will remain in the metastable state (BC) and then return to its initial state B after the field is removed. On the contrary, if a field larger than the coercive field is applied, the polarization will switch to the other state (A′B′) and remain in B′ when the field is suppressed. The vertical dashed lines mark the limits of the quasi steady state hysteresis loop. The evolution of the polarization from a negative polarization state to a positive polarization state in Figure 8(b) is obtained by numerical integration of (7). There is switching only for $E > E_c$. Any field larger than E_c results in the same polarization value. The switching time τ_{in} in intrinsic homogenous switching frame can be defined as the time needed by the polarization from a stable state (e.g., $+P_r$) to cross the zero axis of the polarization (e.g., B → O in Figure 8(a)) [23]. From the relationship between the derivative of the polarization P and the free energy G in (7) and (8) the reciprocal switching time τ_{in} is found to have a square-root critical dependence of the form [86]:

$$\frac{1}{\tau_{\text{in}}} \approx \frac{1}{\tau_0} \left(\frac{E}{E_c} - 1 \right)^{1/2} \left(1 - \frac{T - T_0}{T_1 - T_0} \right)^{1/2}, \qquad (9)$$

where $\tau_0 \approx 6.3\gamma\xi/\beta^2$ and $T = T_0 + 3\beta^2/4\gamma\alpha$. From this equation it can be seen that the switching time τ_{in} will go to infinity as the applied field E approaches E_c or the temperature increases to T_1. There is a true coercive field that for fields below this value no switching should occur. In addition, the temperature dependence of switching process is different from a thermally activated behavior which has an exponential dependence.

Followed by the observation of intrinsic switching in ultrathin P(VDF-TrFE) LB films, several groups argued against the intrinsic nature of the switching [23–27]. In [23] the authors found that the experiments lack several key features of intrinsic switching: the coercive field does not saturate with decreasing film thickness; the electric field and temperature dependence of the switching time are not well described by the intrinsic switching dynamics in (9);

the films have switching below the coercive field. Naber et al. [27] presented measurements using gold electrode for spin coated P(VDF-TrFE) films down to 60 nm. A thickness independence of coercive field is found which leads to the conclusion that the thickness dependence of coercive field in LB films is due to the influence of the electrode interfaces. Very recently, the same group in [21] demonstrated new experiment evidences to confirm the existence of intrinsic switching kinetics in ultrathin ferroelectric copolymer films [28, 29]. They used piezoresponse force microscopy (PFM) to switch the sample at the nanoscale. The dependence of the switching rate on voltage for a 54 nm thick film exhibits extrinsic nucleation and domain growth kinetics without true threshold coercive field and is qualitatively different from the behavior of an 18 nm thick film, which exhibits intrinsic switching kinetics with a true threshold coercive field. The absence of top electrode on the sample can exclude the effect of electrode interface. Intrinsic homogeneous switching is also found in ultrathin ferroelectric $BaTiO_3$ films [30] by PFM and ultrathin epitaxial $PbTiO_3$ films [85] by in situ synchrotron X-ray scattering measurements. Consequently, the authors claimed that homogeneous switching in ultrathin films is a common phenomenon for all ferroelectric materials.

The applicability of these models for PVDF and its copolymer depends on the sample thickness, morphology, external field, and temperature. Up to date, the switching process in P(VDF-TrFE) thin films is not fully understood. Recently, thermal Barkhausen effect is observed in P(VDF-TrFE) copolymer films for the first time [87]. The Barkhausen pulse is a microscopic phenomenon and can be a direct way to prove the existence of domains. The investigation of Barkhausen effect should be a new tool to distinguish different switching mechanisms in ferroelectric materials in the future.

5. Applications

5.1. Nonvolatile Memories. One of the most important applications of P(VDF-TrFE) thin films is ferroelectric nonvolatile memory. The principle of nonvolatile ferroelectric random access memories (FRAMs) is based on the polarization reversal by an external applied electric field. The binary logic

TABLE 1: Comparison of the performances for different types of nonvolatile memories [41–43].

Type	Area/cell (normalized)	Read access time	Write access time	Energy per 32 b write	Energy per 32 b read	Endurance
EEPROM	2	50 ns	10 μs	1 μJ	150 pJ	>10^6
Flash	1	50 ns	100 ns	2 μJ	150 pJ	10^4
FRAMs	2–5	100 ns	100 ns	1 nJ	1 nJ	>10^{15}

states "1" and "0" are represented by the nonvolatile storage of the positive or negative remanent polarization states. The nonvolatile property is due to the fact that the sample can hold the polarization state when the external field is removed. Compared to other nonvolatile memories, for example, flash, electrically erasable and programmable read-only memories (EEPROM) FRAMs have faster write and read times, lower power consumption, and high write and read endurance. A summary of the performances for different devices is given in Table 1. FRAMs can be applied in a variety of consumer products, such as smart cards, power meters, printers, video games, and radio-frequency identification (RFID) tags.

The available commercial FRAMs are based on perovskite-type ferroelectrics such as lead zirconium titanate (PZT) and strontium barium titanate (SBT). Researchers have overcome many difficulties including degradation and retention. Besides, perovskites generally require high annealing temperature (>400°C), which is harmful to other components on the chip. Therefore, the perovskite memory chips require buffer layers and complex mask sets [3, 88]. P(VDF-TrFE) copolymer is the promising material to replace perovskites which has attractive advantages: the device can be achieved by low-temperature processing (<200°C) and solution-processing techniques, which would enable its use in ultra-low-cost applications; the copolymer has outstanding chemical stability which barely reacts to other components and it is nontoxic.

There are three main memory elements based on ferroelectric films: metal-ferroelectric-metal (MFM) capacitor, metal-ferroelectric-insulator-semiconductor (MFIS) diode, and ferroelectric-field-effect-transistor (FeFET). The MFM capacitors can be connected to the transistors to integrate into 1T1C (one-transistor-one-capacitor) or 2T2C (two-transistor-two-capacitor) memory cells [89]. The devices based on MFM capacitors are destructive which require restoration by a rewriting cycle after a readout operation. The MFIS and FeFET devices are nondestructive with the ferroelectric polarization state modulating the electrical conductance of the semiconductor channel and thus distinguishing two logic states.

MFIS devices based on P(VDF-TrFE) films have been investigated by several groups [7–11]. Earlier relatively thick P(VDF-TrFE) films (>100 nm) with SiO$_2$ buffer layer were used resulting in a higher operation voltage (>10 V). More recently, using sub-100 nm P(VDF-TrFE) films, a ±3 V CV loop with a memory window of 1 V was achieved in a stack consisting of 10 nm SiO$_2$ layer and 36 nm P(VDF-TrFE) LB film [9]. A ±4 V loop with a large memory window of 2.9 V was obtained using a 3 nm Ta$_2$O$_5$ buffer layer and a 100 nm P(VDF-TrFE) spin coated film [10]. In [11], the authors

fabricated MFM and MFIS devices using epitaxially grown P(VDF-TrFE) thin films (20–30 nm). A memory window of 2.4 V with a ±5 V loop was obtained in MFIS and their printed micropattern application was demonstrated. All-organic FeFET devices based on P(VDF-TrFE) have been reported in [5, 12–15]. High-performance solution-processed FeFETs were first reported in 2005 by Naber et al. [13] using P(VDF-TrFE) film as the gate insulator and MEH-PPV (poly (2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene)) as a semiconductor. The FeFETs have a long retention time (>one week) with a stable I_{on}/I_{off} of 10^4, a high programming cycle endurance (>1000 cycles), and a short programming time of 0.3 ms. However, with 60 V operation voltages, the devices need to be scaled down. To develop a storage medium that enables an independent tuning of the conductive and ferroelectric properties, Asadi et al. used phase separated films of P(VDF-TrFE) and the polymer semiconductor rir-P3HT (region-irregular poly(3-hexylthiophene)) to realize a nonvolatile resistive memory [90]. The charge injection of the electrode into the semiconducting phase is modified by the poling of the ferroelectric phase. A rectifying diode with a LiF/Al top electrode and a silver bottom electrode can be switched and read out nondestructively. Retention, switching time, and cycle endurance of the blend devices are comparable to those of the state-of-the-art polymer FeFETs. Lately, Gerber et al. [15] fabricated FeFET with very thin P(VDF-TrFE) films prepared by Langmuir-Blodgett technique. The memory element consists of a 10 nm thick SiO$_2$ layer and a 35 nm thick P(VDF-TrFE) film, which can be operated at 4 V. The memory window can also be measured using a Pt/PVDF/SiO$_2$/p-Si gate MFIS stack diode with device capacitance C versus gate voltage V_g, as shown in Figure 9. The high capacitance at negative gate bias is due to accumulation while the low capacitance at positive gate bias arises from depletion. The memory window increases linearly from 0.15 to 1.3 V as the amplitude of the gate voltage cycle increases from ±1 V to ±6 V. In contrast, the memory window decreases with increasing temperature toward the phase transition temperature at a fixed gate voltage cycle (inset in Figure 9). The short retention time (<10 s) is likely limited by incomplete polarization saturation, which can be improved by further reducing the thickness of the oxide layer so that its capacitance is at least ten times that of the ferroelectric film.

In spite of these efforts, to commercialize P(VDF-TrFE) based nonvolatile memory devices, there are two important technical obstacles that must be overcome. First, an appropriate approach must be found to control switching dynamics in the copolymer films. Second, the solution-processing
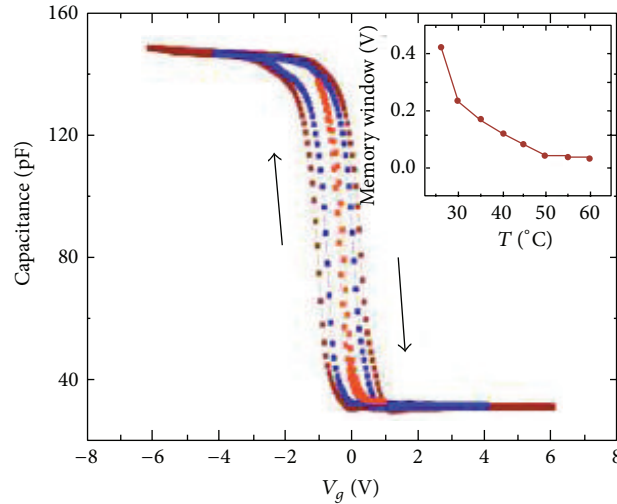
FIGURE 9: Capacitance-voltage hysteresis loops of a Pt/PVDF/SiO$_2$/p-Si gate MFIS stack diode measured with gate voltage sweeps over ±1, ±4 and ±6 V at a rate of 0.05 V/s. The measurement frequency was 100 kHz. The inset shows the width of the memory window as a function of temperature for gate voltage sweeps over ±5 V [15].
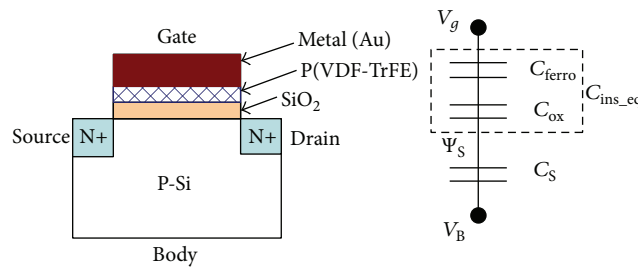

FIGURE 10: Investigated ferroelectric transistor Fe-FET and equivalent capacitive divider of gate potentials [94].

technology must be scaled up and incorporated into the semiconductor-manufacturing process, which is challenge for Langmuir-Blodgett technique [3].

5.2. Negative Capacitance Devices. Conventional field-effect transistors (FETs) require a change in the channel potential of at least 60 mV at room temperature to induce a change in the current by a factor of 10, which is determined by the Boltzmann limit. Recently the concept of coupling the ferroelectric layer to the channel of a field effect transistor for lowering the subthreshold swing due to the negative capacitance effect is actively studied. This concept is proposed by Salahuddin and Datta in 2008 [91] which opens a new route for the realization of transistors with steeper subthreshold characteristics and thus enabling low power dissipation. The experimental validity of Fe-FET with a sub-60 mV/decade switching behavior is firstly demonstrated incorporating a thin P(VDF-TrFE) film into a gate stack [16]. Later, capacitance enhancement is manifested in an epitaxially grown single crystalline bilayer consisting of strontium titanate (SrTiO$_3$) as the dielectric and lead zirconate titanate (Pb$_x$Zr$_{1-x}$TiO$_3$) as the ferroelectric at higher temperature [92] and in an epitaxially grown single crystalline bilayer of SrTiO$_3$ and barium titanate (BaTiO$_3$) at room temperature [93].

Figure 10 shows the device configuration of the negative capacitance FET [94]. The gate insulator consists of a layer of 40 nm P(VDF-TrFe) and a layer of a 10 nm SiO$_2$. The ferroelectric negative capacitance can be stabilized by the in-series positive oxide capacitance. The layer thicknesses and material properties should be properly engineered so as to suppress the hysteretic operation. The gate structure acts as an internal voltage transformer. Thus a small voltage swing on the gate electrode causes a larger change in the internal potential barrier which gates the channel current. The subthreshold swing value depends on the P(VDF-TrFE) thickness and the size of the channel. In this device (channel size of 50 μm × 50 μm) a subthreshold swing as low as 13 mV/decade is measured at room temperature which offers the possibility of lower voltage operation in electronic devices. The challenges include successful integration of ferroelectric/dielectric gate stacks onto FET structures especially for oxides and efficient designs to ensure hysteresis free operation [95]. More works need to be done including temperature and interface effect on the device performance.

5.3. Photovoltaic Devices. Recently it is reported that, by using a permanent electric field of an ultrathin layer of ferroelectric P(VDF-TrFE) introduced at the interface between
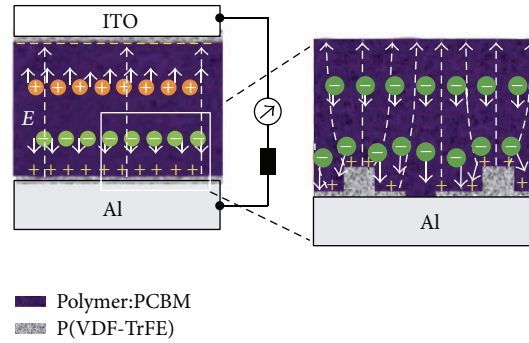
FIGURE 11: The structure of polymer photovoltaic devices with FE interfacial layers and a schematic diagram of electric field induced by the polarized FE layer and the field-assisted charge extraction. The right-hand panel illustrates the electric-field distribution and electron conduction through the P(VDF-TrFE) on the Al side [17].

the electrode and a semiconductor layer in an organic photovoltaic (OPV) device, the charge pair separation and charge extraction efficiency can be increased and thus the power conversion efficiency (PCE) is enhanced by up to 200% [17, 96]. OPV devices have been intensively investigated during the last few years due to their promising application for future low cost and high performance energy sources. The energy loss in OPV devices is mainly caused by the recombination of electrons and holes in semiconducting polymer-fullerene blends. To separate the electrons and holes and prevent their recombination by an external field is essential to increase the OPV efficiency. A large internal electric field can be induced by incorporating a ferroelectric layer thus eliminating the need for an external field. The device structure and working principle of the OPV based on a P(VDF-TrFE) thin film are illustrated in Figure 11. The ultrathin ferroelectric layer was prepared by Langmuir-Blodgett technique and inserted at the interface of the organic semiconducting layer and metal electrode, which has a large polarization of the order of $10\,\mu C/cm^2$. The ferroelectric layer can induce a high density of charges at the FE-semiconductor interface which cannot be compensated by the low-concentration free charges in organic semiconductors. The built-in electric field introduced by the P(VDF-TrFE) layer is derived as $E = d\sigma_P/\varepsilon_0\varepsilon_{FE}L$, with σ_P being the polarization charge density, d the thickness of the P(VDF-TrFE) layer, L the thickness of the polymer semiconductor layer, and ε_{FE} the relative dielectric constant of the P(VDF-TrFE) layer. A three monolayer (5 nm) P(VDF-TrFE) film can induce an internal built-in field as high as $50\,V/\mu m$ in a 150 nm $P3HT:PC_{70}BM$ layer and thus suppresses the recombination in the device. According to the above derived equation, the higher the built-in electric field is, the thicker the P(VDF-TrFE) layer is. However, the increase of the P(VDF-TrFE) layer thickness also increases the contact resistance, which would reduce device efficiency [17]. The authors found that one or two monolayers of P(VDF-TrFE) were the optimum thickness range for $P3HT:PC_{70}BM$ to achieve the highest efficiency.

5.4. Multiferroic Tunnel Junctions. Incorporating P(VDF-TrFE) thin films in multiferroic tunnel junctions is also an emerging application. Ferroelectric polymer has a high electric

polarization and weakly binds to the metal ferromagnets, which are favorable for use as barriers in multiferroic tunnel junctions. Experimentally, Mardana et al. have demonstrated that the use of P(VDF-TrFE) LB films can efficiently tailor the interface magnetocrystalline anisotropy (MCA) of an adjacent ferromagnetic Co layer [18]. In a wedge-shaped Co film of varying thickness overlaid with a P(VDF-TrFE) film the magnetic anisotropy of the Co films changes as much as 50% when the ferroelectric polarization of the copolymer is switched from up to down. The large mismatch in the stiffness coefficients between the copolymer and the metal ferromagnet manifests that the magnetic changes are caused by the large electric field at the ferroelectric/ferromagnet interface. First-principles density functional calculations [97, 98] show that PVDF based multiferroic tunnel junctions have very high tunability of the tunneling magnetoresistance and electroresistance effects, which are promising candidates for logic and memory applications. More experiment works need to be done.

6. Summary and Outlook

Significant advances have been made on the development of ferroelectric devices based on PVDF and P(VDF-TrFE) thin films in the last ten years. Still, we are in the early stages of commercialization of thin ferroelectric polymer devices in organic electronics. There remain some questions about the microscopic mechanisms of polarization reversal in ferroelectric polymer films. Understanding of these issues is critical. The material quality in terms of processing and properties could be evaluated and improved. Future works to establish a clear relationship between ferroelectric properties and device performance are required. The prospects of ferroelectric polymer devices are promising for microelectronic industry.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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