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# Low voltage extrinsic switching of ferroelectric $\delta$ -PVDF ultra-thin films

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Non-volatile memories operating at low voltage are indispensable for flexible micro-electronic applications. To that end, ferroelectric  $\delta$ -PVDF films were investigated as a function of layer thickness down to 10 nm ultra-thin films. Capacitors were fabricated using PEDOT:PSS as non-reactive electrode. Full polarization reversal was obtained at an unprecedented voltage below 5 V. The remanent polarization of  $7 \mu\text{C}/\text{cm}^2$  and coercive field of 120 MV/m are independent of layer thickness, demonstrating that ferroelectric switching in  $\delta$ -PVDF is extrinsic, dominated by inhomogeneous nucleation and growth. The ease of processing of  $\delta$ -PVDF allowed to determine a lower limit of the critical ferroelectric thickness. © 2013 AIP Publishing LLC.

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Organic electronics has emerged as a promising technology for large-area micro-electronic applications such as electronic paper,<sup>1</sup> smart labels,<sup>2</sup> rollable displays,<sup>3</sup> and contactless identification transponders.<sup>4</sup> Most of these applications require memory functions, preferably a non-volatile memory that retains its data when the power is turned off, and that furthermore can be programmed, erased, and read-out electrically. Ferroelectric polymers are the ideal candidate for switching as they exhibit an intrinsic bistable, remanent, polarization,  $P_r$ , which can be switched by an electric field. The remanent polarization can adopt either of two stable polarization states. Switching from one polarization state to the other can occur by applying an electric field that exceeds the coercive field,  $E_c$ .

The most commonly used organic ferroelectric is the random copolymer of vinylidene fluoride with trifluoroethylene (P(VDF-TrFE)). The coercive field depends on the trifluoroethylene content.<sup>5</sup> For the copolymer ratio of 65/35 the coercive field is about 50 MV/m and for the ratio of 80/20 the field is about 80 MV/m.<sup>6</sup> Hence to obtain switching voltages below 10 V sub-100 nm films are required. It is now well-established that reproducible switching can be realized, but only down to 50 nm thin films. For those films the remanent polarization and coercive field are independent of layer thickness.<sup>7</sup> The switching times are independent of film thickness as well.<sup>8</sup> Fabrication of thinner films of P(VDF-TrFE) is hampered by the required thermal annealing at about 140 °C in order to enhance the crystallinity and hence the ferroelectricity. The thermal annealing promotes grain growth and leads to inherently rough surfaces and electrically shorted capacitors. In ultra-thin films, thermal annealing can even cause dewetting. Therefore, not surprisingly, for P(VDF-TrFE) thin films there is a large scatter in switching voltages, remanent polarization, and coercive field.

Recently, ferroelectric  $\delta$ -PVDF (poly(vinylidene fluoride)), an overlooked polymorph proposed 30 years ago, has been reported.<sup>9</sup> This  $\delta$ -phase is obtained upon electro-

forming by applying a short electrical pulse on a neat PVDF film. For practical applications, the advantage of the homopolymer  $\delta$ -PVDF over the copolymer P(VDF-TrFE) is the high thermal stability of the polarization due to the high Curie temperature of about 170 °C; however, an issue could be the high value of the coercive field of about 120 MV/m. To realize low voltage switching, crucial for any micro-electronic application, ultra-thin films are required. Fortunately, thin  $\delta$ -PVDF films can easily be made because thermal annealing is not needed during the whole fabrication. The large processing window makes  $\delta$ -PVDF the ideal candidate to achieve low voltage switching and, at the same time, to study the ferroelectric properties as a function of layer thickness down to ultra-thin films. Here we show that ultra-thin films down to 10 nm of  $\delta$ -PVDF can be fabricated. The surface roughness is less than 1 nm. The remanent polarization of  $7 \mu\text{C}/\text{cm}^2$  is switched with an unprecedented low bias of less than 5 V. We note that the ferroelectric switching mechanism can be extrinsic, driven by inhomogeneous nucleation and growth, or intrinsic by a coherent, collective rotation of the dipoles.<sup>10</sup> A distinction can be made from the thickness dependence of coercive field and remanent polarization. The data presented here for PVDF films from thick films of 1 micron down to ultra-thin films of 10 nm can identify the switching mechanism and unambiguously set a lower limit for the critical ferroelectric thickness.

PVDF (180 kg/Mol, Sigma-Aldrich) was dissolved in N, N-dimethylformamide (DMF). Thin films were fabricated by spin-coating. The layer thickness was controlled by varying the solid weight content or spinning speed and measured with a surface profilometer. The surface roughness is dominated by the relative humidity. Smooth thin films can be fabricated by either spin-coating at elevated temperature, at about 100 °C, in ambient air or at room temperature in a nitrogen glove box. Capacitors were fabricated on thermally oxidized silicon monitor wafers on which 50 nm thick Au bottom electrodes on a 2 nm Ti adhesion layer were photolithographically defined. Ultra-thin PVDF films were deposited on top. To prevent electrical shorts the conducting

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polymer poly(ethylene dioxythiophene) stabilized with poly(styrene sulfonic acid) (PEDOT:PSS) was used as a top electrode.<sup>11</sup> To prevent dewetting of PEDOT:PSS on the hydrophobic PVDF film a few drops of the nonionic Zonyl FSO-100 (DuPont) fluoro-surfactant were added to the waterborne PEDOT:PSS suspension (PH500, Heraeus). The PEDOT:PSS thickness amounted to 100 nm, and the conductivity was 300 S/cm. On top of the PEDOT:PSS Au was evaporated through a shadow mask. The capacitors were finished by removing the redundant PEDOT:PSS with reactive ion etching using the previously deposited Au patterns as a self-aligned mask. The device area varied from 0.059 to 1.38 mm<sup>2</sup>. Electric displacement loops versus electric field were measured using a Sawyer-Tower circuit, consisting of a Tektronix AFG3102 function generator, a LeCroy waverunner LT372 oscilloscope, and a Krohn-Hite 7602M wide band amplifier. The capacitors were measured with a continuous triangular wave signal, to reduce the time at maximum bias, at a frequency of 100 Hz, using a reference capacitor of 68 nF.

Fig. 1 shows the film thickness (blue symbols, left axis) and the rms roughness (red symbols, right axis) of the neat films as a function of PVDF weight content in the solution. The films are extremely smooth. The roughness of the ultra-thin films is less than 1 nm. The film thickness increases linearly with weight content. The superlinear increase at high weight content could be due to the increased viscosity. AFM measurements and optical micrographs showed that the as-cast films contain relatively large spherulites of up to 10  $\mu$ m, typical for microcrystalline  $\alpha$ -PVDF. A typical AFM height image of a 117 nm thin film is presented in the inset of Fig. 1. The crystals are strongly structured, with bifurcating branches growing from the nucleating center outwards to the front.

According to X-ray diffraction measurements, as-deposited films crystallize in the non-polar  $\alpha$ -phase. Comprising capacitors are paraelectric. Upon electro-forming by applying a short electrical pulse of about 250 MV/m, ferroelectric  $\delta$ -PVDF, or more appropriately polar  $\alpha_p$ , is formed out of the non-polar  $\alpha$ -PVDF pristine film. After electro-forming the ferroelectric hysteresis loops were

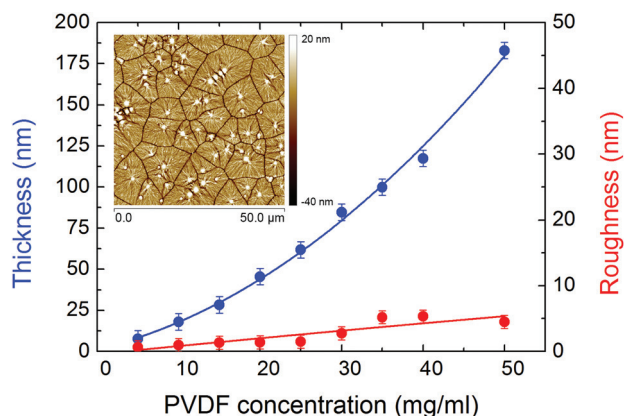


FIG. 1. Topography of as-deposited PVDF thin films. The layer thickness and rms roughness are obtained from surface profilometer measurements. The blue symbols present the film thickness as a function of solution concentration (left axis). The red symbols present the corresponding film roughness (right axis). The error bars are obtained by averaging over 5 films. The solid lines are a guide to the eye. The inset is a typical AFM height image of a PVDF film with a thickness of 117 nm.

measured. The displaced charge density as a function of applied bias is presented in Fig. 2(a) for the full set of PVDF capacitors with different thicknesses. The films are ferroelectric down to the thinnest film investigated here of 18 nm. The full polarization reversal then occurs at a bias less than 5 V. We note that after electro-forming the ferroelectric properties were fixed; they did not change upon application of subsequent, second poling pulse. The yield for films with a thickness of about 50 nm or more is unity. The yield for ultra-thin films is an order of magnitude lower but acceptable taking into account that processing was not carried out in a cleanroom.

The displacement current versus voltage curves of Fig. 2(a) are replotted as a function of applied field in Fig. 2(b). All hysteresis loops then collapse, demonstrating that the remanent polarization and the coercive field do not depend on layer thickness. The remanent polarization is 7  $\mu$ C/cm<sup>2</sup> and the coercive field around 120 MV/m. A similar conclusion can be drawn from Fig. 3 where the forming voltage,  $V_f$ , and the coercive voltage,  $V_c$ , are presented as a function of layer thickness. A linear relation is found showing that both the forming field of 250 MV/m and the coercive field are independent of layer thickness.

Electro-forming of  $\delta$ -PVDF from  $\alpha$ -PVDF requires rotation of every other second chain over 180° and a translation of that chain over half the  $c$ -axis lattice constant.<sup>9</sup> In

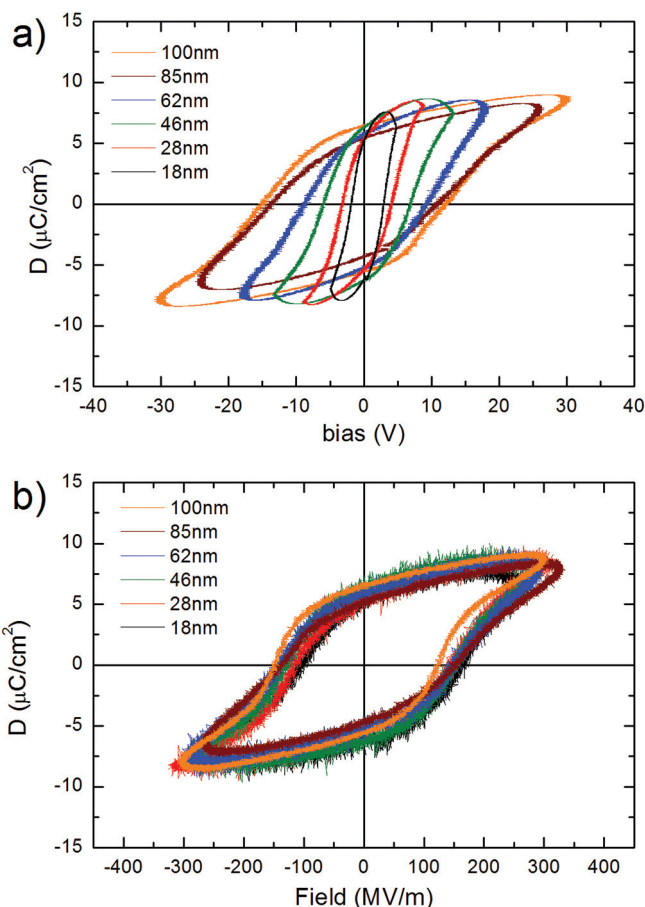


FIG. 2. Saturated hysteresis loops for various film thicknesses. The displaced charge density is presented as a function of applied (a) bias and (b) electric field. All capacitors yielded the same remanent polarization,  $P_r$ , and coercive field,  $E_c$ , with a layer thickness ranging from 100 to 18 nm.

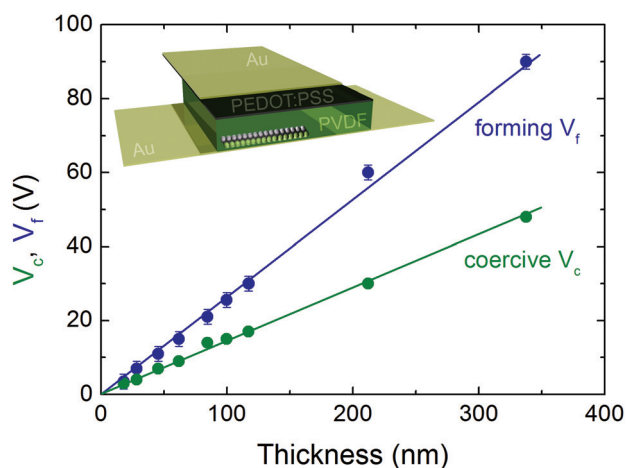


FIG. 3. Scaling of  $\delta$ -PVDF. Forming voltage,  $V_f$ , and coercive voltage,  $V_c$ , of  $\delta$ -PVDF are presented as a function of layer thickness. The linear relation found yields a forming field of  $250 \text{ MV m}^{-1}$  and a coercive field of  $120 \text{ MV m}^{-1}$ . The inset shows the capacitor layout.

contrast, ferroelectric switching involves only rotation of the polymer chains. Hence the electro-forming field is much higher than the coercive field, as shown in Fig. 3. It explains that the formation of  $\delta$ -PVDF from  $\alpha$ -PVDF is irreversible and that the  $\delta$ -phase is stable under repetitive switching.

The switching mechanism of organic ferroelectrics is under debate since the publication of switching in ultra-thin Langmuir-Blodgett (LB) films of P(VDF-TrFE).<sup>12</sup> The switching can be either extrinsic or intrinsic.<sup>10</sup> Extrinsic switching is nucleation driven. The switching occurs through inhomogeneous nucleation of small domains with reversed polarization, followed by growth of these domains accompanied by domain wall motion. When the switching is intrinsic the nucleation is suppressed. The dipoles are highly correlated and switch either coherently or not at all. The signature of extrinsic switching is a coercive field and switching time that is independent of layer thickness, while intrinsic switching is characterized by a coercive field that increases with decreasing layer thickness and eventually saturates, and a switching time that dramatically increases with decreasing layer thickness. Reported values for the coercive field of P(VDF-TrFE) as a function of layer thickness are presented in Fig. 4(a).<sup>12–21</sup> A large scatter in the data is obtained. The spread in data points is partly due to the use of reactive metals as electrodes. Numerous studies have shown that the coercive field increases and the remanent polarization decreases with decreasing layer thickness.<sup>12,21–23</sup> Dielectric relaxation measurements have shown that the origin is a dead surface layer due to the use of reactive metals such as Al (Ref. 8) that artificially enhance the extracted values of the coercive field. To circumvent electrode passivation, capacitors have been made using non-reactive metals such as Au or PEDOT:PSS. It is now well-established that down to 50 nm the coercive field and switching time do not depend on the layer thickness. The switching is then extrinsic. Whether intrinsic switching occurs for thinner films of P(VDF-TrFE) is open for debate. Experimental investigation is hampered by dewetting upon thermal annealing.

The coercive field extracted for  $\delta$ -PVDF as a function of layer thickness is presented in Fig. 4(b). Down to the thinnest

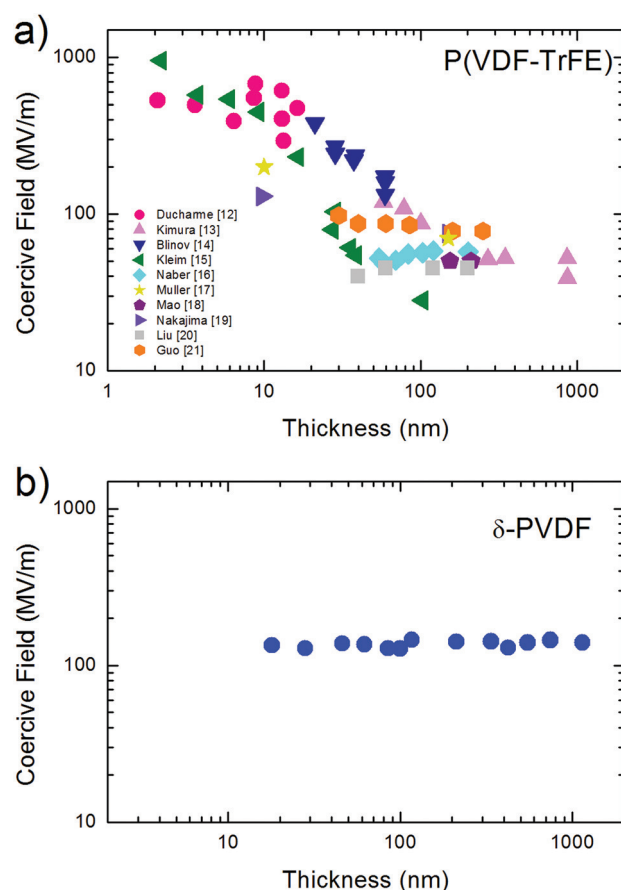


FIG. 4. Scaling of coercive field with layer thickness. (a) Literature data reported for the coercive field of P(VDF-TrFE). The values were extracted from Refs. 12–21. (b) Present results of coercive field for  $\delta$ -PVDF with a layer thickness from 1  $\mu\text{m}$  to about 10 nm.

films investigated the coercive field is constant. Ferroelectric switching in  $\delta$ -PVDF is therefore extrinsic, and we obtain a lower limit for the occurrence of intrinsic switching, if any, of 18 nm.

In summary, we have fabricated ultra-thin smooth films of neat PVDF. The surface roughness is less than 1 nm for 10 nm thick films. Upon electro-forming by applying a short electrical pulse, ferroelectric  $\delta$ -PVDF is formed. The forming field does not depend on layer thickness and amounts to  $250 \text{ MV/m}$ . Ferroelectric hysteresis loops were measured as a function of thickness. Contrary to the copolymer P(VDF-TrFE),  $\delta$ -PVDF is experimentally accessible because thermal annealing is not needed, and, therefore, dewetting of the as-deposited films can be avoided. Full polarization reversal of  $\delta$ -PVDF was obtained for ultra-thin films at an unprecedented voltage below 5 V. The remanent polarization of  $7 \mu\text{C/cm}^2$  and the coercive field of  $120 \text{ MV/m}$  are independent of layer thickness, which implies that in these films the ferroelectric switching is extrinsic, dominated by inhomogeneous nucleation and subsequent growth. The data are compared with that of the copolymer P(VDF-TrFE). For neat PVDF, a lower limit of 18 nm is extracted for the critical thickness where a cross-over to intrinsic switching might occur.

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