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Low voltage switching of a spin cast ferroelectric polymer

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Employing a conductive polymer as the bottom electrode material of a ferroelectric capacitor is shown to improve the ferroelectric properties of sub-100-nm-thick spin cast poly(vinylidene fluoride/trifluoroethylene) copolymer insulator films. It is demonstrated that a remanent polarization of 65 mC/m² is switched with only 5.2 V (80 MV/m) with a switching time of 80 ms. Compared to similar capacitors but with an aluminum bottom electrode the main improvement is a reduction of the switching time with 3 orders of magnitude at this field strength. © 2004 American Institute of Physics. [DOI: 10.1063/1.1788885]

The ferroelectric poly(vinylidene fluoride/trifluoroethylene) [P(VDF/TrFE)] copolymers have been proposed for use in low cost, large area solid state electronic memories.¹ Their ease of processing through spin casting would be ideal when combined with low voltage operation. Due to the relatively high coercive field (E_c) of 50 MV/m sub-100-nm thick ferroelectric layers are required in order to attain an operation voltage below 10 V. A paper regarding the thickness scaling of polymer based ferroelectrics reported an increase in both coercive field and switching time with decreasing layer thickness.² A number of studies dealing with this issue followed.^{3–7} An overview of remanent polarization (P_r) values versus ferroelectric layer thickness is shown in Fig. 1. Note that the polarization also depends on the copolymer ratio of the copolymer used so only changes relative to thick film values are relevant.

The decline of curves 1–3 below 100 nm has been attributed to a reduction of crystallinity, as determined by x-ray diffraction experiments.^{3–5} P(VDF/TrFE) films are semicrystalline and the ferroelectricity originates from the crystalline phase. Curves 3–5 indicate a downward shift of this apparent critical thickness from 100 to 70 nm. Using an annealing temperature lower than the standard 140°C resulted in less decline of the remanent polarization, e.g., 30% P_r decline at 40 nm instead of 50% at 60 nm.⁵ This was explained by an improved crystallization due to a reduction of the crystal lamellar size. In contrast to these results, curves 6 and 7 show even less decline, e.g., only 10% at 50 nm.^{6,7} Instead of optimizing on annealing conditions this small decline is most likely due to the differing measurement procedures. Curve 6 was obtained with unusually high fields exceeding 300 MV/m. Curve 7 was measured using common field strengths of about 100 MV/m but with field application times exceeding seconds. As the switching time depends exponentially on the applied field,⁸ these results are mutually consistent and suggest that it is mainly the switching time that is affected by the layer thickness decrease. The paper describing curves 3–5 does not mention the timescale at which the remanent polarizations were obtained.⁵ This prevents a direct comparison of the literature values. Regardless, the challenge put forward is not only the retainment of the P_r

of the bulk material in sub-100-nm thick films, but also the preservation of the switching time.

It has been demonstrated that the use of polymeric electrodes lead to an improvement in the performance and stability of light-emitting diodes based on conjugated polymers.⁹ The improvements have been attributed to better adhesion and wetting as compared to metallic electrodes. The present study is about the benefits of using a conductive polymer as opposed to aluminum for the bottom electrode of ferroelectric capacitors. All the abovementioned results were obtained on capacitors that had transition metal or aluminum bottom electrodes.^{3–7} Employing a polymeric bottom electrode we demonstrate an almost unaffected P_r , E_c and switching time (t_{sw}) behavior down to at least 65 nm P(VDF/TrFE) layer thickness. This enables switching of 65 mC/m² with 5.2 V (80 MV/m) while the switching current peaks at only 80 μ s (the full switching event is completed within 400 μ s).⁷

Metal–P(VDF/TrFE)–metal capacitors were made with aluminum or an indium–tin–oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonicacid) (PEDOT:PSS) stack as the bottom electrode. Good comparability between both types of capacitors was obtained by using the same deposition procedure for both the ferroelectric

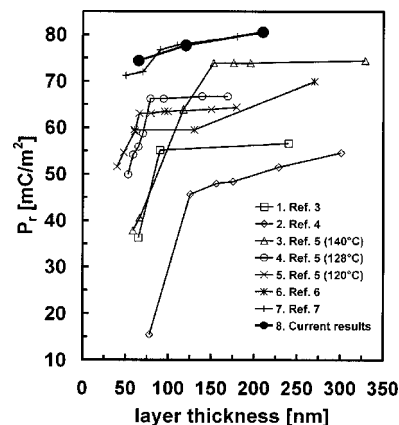


FIG. 1. Summary of the remanent polarization of spin cast P(VDF/TrFE) capacitors as a function on the ferroelectric layer thickness. The graph includes reported as well as present results. The lines are drawn as a guide to the eye.

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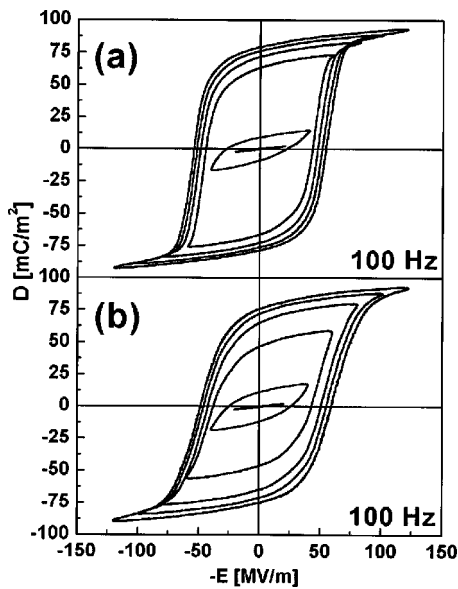


FIG. 2. Displacement charge D vs applied field E hysteresis loop measurements using a standard Sawyer–Tower circuit at a frequency of 100 Hz. Several field strengths are included to show at what fields the ferroelectric polarization appears and saturates. The capacitors used have a PEDOT bottom electrode. The ferroelectric layer thicknesses are (a) 210 nm and (b) 65 nm.

thin film and the gold top electrode. The ITO electrodes were sputtered and lithographically patterned. The aluminum electrodes were deposited by shadow mask evaporation. PEDOT:PSS (Baytron® P) was applied onto the ITO containing substrates by spin casting, dried at 140°C, washed with 2-butanone and dried again. The P(VDF/TrFE) random copolymer with 80 mol% VDF (Solvay Duphar, Belgium) was subsequently spin cast at 1000 rpm from filtered 2-butanone solutions. The layer thickness was varied by concentration adjustment and verified with profilometer measurements. The P(VDF/TrFE) films were annealed in a vacuum oven at 138°C for 2 h to enhance the crystallinity. Finally, gold top electrodes were evaporated through a shadow mask resulting in capacitor surface areas in the range of 7–16 mm². For the ferroelectric characterization, Sawyer–Tower charge displacement versus applied field (D – E) hysteresis loops were measured. The resulting P_r values were verified with voltage pulse measurements, in which it is assumed that the dielectric and leakage contributions to the charge displacement are the same for switching and non-switching pulses and can therefore be eliminated.⁵ The D – E measurements were followed by switching time measurements. These were carried out using a published method in which the samples are abruptly connected to a large, charged capacitor using a mercury switch.⁸

Typical D – E hysteresis loops from our PEDOT based capacitors with P(VDF/TrFE) thicknesses of 210 and 65 nm are shown in Figs. 2(a) and 2(b). The 210 nm film represents the bulk ferroelectric properties whereas the 65 nm films represent a film thickness below the critical thickness of 100 nm of Fig. 1. Both capacitors show square and symmetrical hysteresis loops. They both saturate at 120 MV/m, resulting in a P_r of about 75 mC/m² and an E_c of 55 MV/m. The P_r values obtained are included as fully closed circles in Fig. 1. Comparison with the literature data in Fig. 1 shows that the remanent polarization of the capacitors are almost independent of the layer thickness. We note that we neither had to

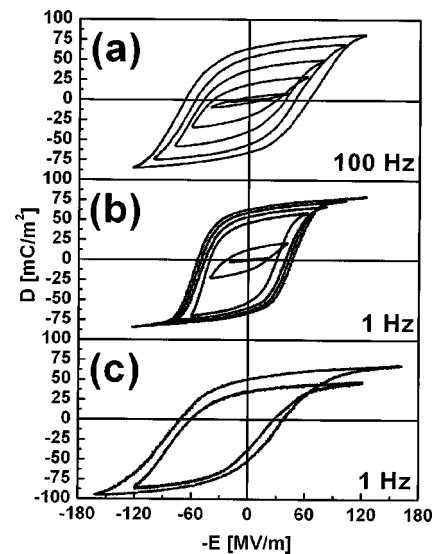


FIG. 3. D – E hysteresis loop measurements equivalent to Fig. 2 except that the bottom electrode material is aluminum instead of PEDOT: (a) obtained with a 190 nm ferroelectric layer thickness and 100 Hz frequency; (b) the same as (a) but at 1 Hz; (c) obtained with a ferroelectric layer thickness of 60 nm and a frequency of 1 Hz.

change the annealing procedure nor had to apply unusually high or long electric fields to obtain these results.

In order to investigate the origin of the improved thickness scaling behavior capacitors with Al bottom electrodes were also investigated. The hysteresis loops measured as a function of thickness and scanning frequency are presented in Fig. 3. Comparison between Figs. 3(a) and 3(b) shows that for thick films of 190 nm ferroelectric saturation occurs at a lower electric field when the scanning frequency is decreased from 100 to 1 Hz. The hysteresis loops scanned at 1 Hz [Fig. 3(b)] resemble the loops of the PEDOT devices at 100 Hz (Fig. 2). We can therefore conclude that the switching time behavior of the Al based capacitors is inferior to the PEDOT based capacitors. Fig. 3(c) then shows hysteresis loops of aluminum based capacitors using a 60 nm thin P(VDF/TrFE) film at a frequency of 1 Hz. Saturation occurs only at higher fields, i.e., 160 instead of 120 MV/m. Figure 3(c) shows an asymmetry in coercive fields which is largely due to the built-in field (E_{bi}) caused by the difference in metal work functions (Φ) of the top and bottom electrodes.¹⁰ The $\Delta\Phi$ of about 0.83 eV and the 60 nm film thickness results in an E_{bi} of 14 MV/m.¹¹ The bulk E_c of 55 MV/m plus or minus this value corresponds to the observed E_c values of –73 and 36 MV/m. Figure 3(c) also shows that the hysteresis loops saturate at lower fields on the right-hand side than on the left, which suggests a dependence of the switching time upon the sign of the applied field. The P_r value of 50 mC/m² is a lower limit because full saturation does not occur. We note that it is 30% higher than the corresponding literature value in Fig. 1, curve 3. This indicates that the P_r decline with thickness decrease is smaller in our devices. We therefore focus on how the switching time depends upon the bottom electrode material.

Switching time measurements were performed in order to quantify the temporal behavior of the polarization. t_{sw} is defined as the time between the start of an applied voltage pulse and a peak maximum of $\partial D / \partial \log(t)$.⁸ The switching times for capacitors with various layer thicknesses are pre-

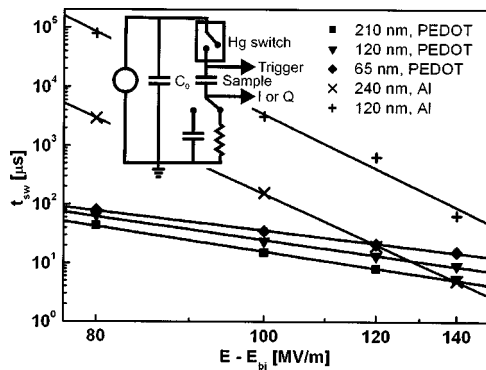


FIG. 4. Switching time, t_{sw} , as a function of the field strength of an applied voltage pulse. t_{sw} is defined as the time between the start of the pulse and a peak maximum of $\partial D/\partial \log(t)$. The inset shows a schematic of the experimental setup (Ref. 8). The applied field was corrected for the expected built-in field. For devices with Al and Au it is calculated as 0.83 V divided by the P(VDF/TrFE) layer thickness. The small difference between the work functions of PEDOT and Au is neglected. The lines are drawn as a guide to the eye.

sented as a function of electric field in Fig. 4. The inset depicts the measurement scheme.⁸ The 100 MV/m data points show that a 120 nm thick P(VDF/TrFE) layer on PEDOT switches 100 times faster than the same layer on Al. At 80 MV/m this ratio becomes 1000. This confirms our observation that ferroelectric saturation in 100 Hz hysteresis loops appears at higher fields for Al devices than for PEDOT devices. It is because the field at that frequency is not applied long enough for full polarization to occur. Our switching time results for Al based devices are similar to those reported by Tajitsu.⁷ In both studies the switching times increase with decreasing ferroelectric layer thickness in a similar way. Figure 4 also shows that the switching time of Al based devices decreases more with increasing field than PEDOT based devices. The difference with PEDOT based devices becomes negligible above 140 MV/m. Why the switching time of PEDOT based capacitors is less dependent on the applied field is not yet clear. The RC time of the circuit could theoretically limit t_{sw} but it was measured to be 0.2–0.5 μs (depending on sample thickness), which is nearly 2 orders of magnitude shorter than the actual switching times observed.

The strong dependence of the ferroelectric properties of P(VDF/TrFE) thin films upon the type of electrode agrees with recent observations by Xia *et al.* They used both Al and Ni electrodes for capacitors with a thickness of 200 nm.¹² The Ni capacitor, measured at a 150 MV/m scanning field, was shown to have a higher P_r than the Al capacitor measured at 200 MV/m. A thin insulating layer of Al_2O_3 on the bottom electrode of the Al based capacitors could reduce the applied field on the ferroelectric. However, such a layer would be ~ 2 nm thick and using a P(VDF/TrFE) layer of

60 nm thickness this effect can only lead to a negligible reduction of the applied field. Hence, the formation of a thin Al_2O_3 layer alone cannot account for the strong decrease of the ferroelectric properties. The large role of the bottom electrode was also demonstrated by results from 20 to 50 nm thick films spin cast onto graphite.¹³ After applying a voltage bias, either a low or a high piezoelectric response was obtained from these films, depending on the sign of the applied bias. This was explained in terms of a parallel or antiparallel polarization with respect to an oriented polymer layer induced by the bottom interface, the orientation of which is insensitive to the applied field. Whether such a fixed dipole layer is also the cause of the inferior switching time behavior of Al based capacitors is a subject of further study.

In summary, D - E hysteresis loops of ferroelectric capacitors with PEDOT bottom electrodes and spin cast P(VDF/TrFE) copolymer layers were shown to saturate at lower electric fields and higher scanning frequencies than aluminum based capacitors, especially when the ferroelectric layer thickness is below 100 nm. Switching time measurements indicate that the main cause of this difference lies in the ferroelectric switching time at commonly used field strengths of 80–140 MV/m. Utilization of PEDOT electrodes enables the combination of an operation voltage of only 5.2 V with a remanent polarization and switching time behavior similar to that of bulk P(VDF/TrFE). This improvement enables the use of ferroelectric polymers in non-volatile memories operating at low voltage.

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