RAPID COMMUNICATIONS

PHYSICAL REVIEW B **92**, 060102(R) (2015)

Homogeneous switching mechanism in pure polyvinylidene fluoride ultrathin films

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(Received 4 May 2015; revised manuscript received 25 July 2015; published 26 August 2015)

Polarization switching kinetics is one of the key issues for future development of nanoelectronic devices based on ferroelectrics. Up to now, such kinetics still remains poorly studied despite its crucial impact on the device performances. Here, the switching mechanism in 11-nm-thick ferroelectric films of pure homopolymer of polyvinylidene fluoride is investigated. While the usual mechanism involves nucleation and growth of domains, a homogeneous ferroelectric switching is evidenced in such ultrathin films. Indeed, the dependence of the switching rate on applied voltage reveals a critical behavior with the existence of a true threshold field (of ∼0.26 GV/m) which is required to overcome the energy barrier to reverse the whole polarization homogeneously as suggested by Landau-Ginzburg mean-field theory. Such finding not only supports few previous works but also raises the question on the general aspect of such homogeneous mechanism that might exist in any other nanoscale ferroelectric materials.

DOI: 10.1103/PhysRevB.92.060102 PACS number(s): 77.80.Fm, 61.41.+e, 68.47.Pe, 81.05.Lg

In a ferroelectric material the polarization can be switched between two stable states by an external electric field and the switching is accompanied by a hysteresis loop in terms of the polarization versus the applied field. From the early studies on the kinetics of switching in ferroelectric crystals [1–5], it has been understood that polarization switching is generally a complex inhomogeneous process referred to as extrinsic switching and involves reversed domain nucleation and their growth. However, in the ultrathin films, this extrinsic switching might be suppressed because the nucleation is inhibited as the reduced film thickness limits nucleation volume. Therefore, the study and modeling of the polarization switching becomes central when downscaling and of great importance for applications of ferroelectric films into nanoelectronics such as logic devices and memories [6].

Interestingly, Ducharme *et al.* [7] and Vizdrik *et al.* [8] proposed that in ultrathin films the switching kinetics follows a homogeneous mechanism that can be derived from Landau-Ginzburg (LG) mean-field theory [7,8]. According to LG theory [9,10], if an electric field is large enough to overcome the energy barrier associated with the long-range correlation of the polarization, the polarization state can switch homogeneously, without the nucleation and growth domain process. Such mechanism where all the dipoles in a given domain switch coherently all together is called intrinsic or homogeneous switching. As a result, while an exponential dependence on reciprocal electric field is expected for extrinsic switching kinetics, the switching rate in the case of intrinsic switching should display a critical dependence on electric field [8]. Actually, intrinsic switching was first reported in polyvinylidene fluoride-trifluoroethylene [P(VDF-TrFE)] copolymer films when the thickness is lower than 15 nm [7,8,11,12]. The TrFE compound is typically added in order to stabilize the all-*trans* ferroelectric β phase in such polymers.

Recently, advances in the fabrication of polymer nanostructures [13] allow one to obtain pure polyvinylidene fluoride (PVDF) homopolymer thin films with very good ferroelectric quality by using layer-by-layer Langmuir-Blodgett (LB) technology [14]. Note that similarly, efforts in the growth of oxide-based epitaxial ferroelectric films with thickness less than 10 nm have been also achieved. Consequently it has been also suggested that an intrinsic switching mechanism in such inorganic ferroelectric films [15–17] such as, e.g., lead titanate and barium titanate could occur. In pure PVDF, it was proposed that a transition from extrinsic to intrinsic switching happens for a thickness ranging between 45 and 11 nm [14]. Bystrov investigated the switching kinetics of PVDF films at nanoscale using a molecular dynamics simulation method and predicted that the polarization switching should show a homogeneous critical behavior around the coercive field derived from LG theory [18]. However, despite continuous efforts, experimental evidence of homogeneous polarization switching kinetics in ultrathin PVDF films is still lacking until now. In the present study, we perform a direct measurement of current versus voltage (*I-V*) curves in a capacitance made with 11-nm-thick ferroelectric PVDF film. The dependence on voltage of the switching rate exhibits a critical behavior associated with the existence of a true threshold field as expected from LG theory for homogeneous switching. We therefore provide clear experimental evidence demonstrating that such mechanism is dominating the polarization switching in ultrathin (11 nm) ferroelectric films made of pure PVDF.

Five transferred layers of pure PVDF (with molecular weights of 180 275, purchased from Sigma-Aldrich) were deposited uniformly by using a horizontal LB technology (Nima 611) on the Au-coated Si, as described in Ref. [14].

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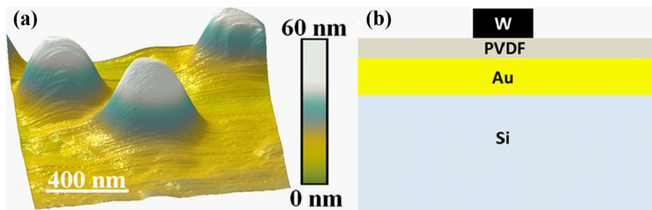

FIG. 1. (Color online) Sketch of the devices: (a) AFM topography showing three nanocapacitors. (b) Schematic of a tungsten/PVDF/gold nanodevice on a Si substrate.

The final film thickness determined by variable-angle spectroscopic ellipsometry analysis is about 11 nm, in agreement with Ref. [14]. Tungsten (W) was deposited onto the film through an electron-beam-induced deposition method to form an Au-PVDF-W capacitor structure. A sketch of the structure is presented in Figs. 1(a) and 1(b). Figure 1(a) displays atomic force microscope (AFM) topography of three nanodevices, while Fig. 1(b) depicts the side view of one specific nanodevice. These devices were annealed at 110 °C for 0.5 h in air to improve the crystallinity. Every capacitor looks finally like a rounded pad with a lateral diameter of about 400 nm.

The ferroelectricity character of the 11-nm-thick film was checked by piezoresponse force microscopy (PFM). As shown in Fig. 2 (right), a slanted but typical out-of-plane PFM phase hysteresis loop is obtained and the value of the coercive voltage (~3 V) agrees well with our earlier work in which we performed polarization electric field (*P-E*) loops directly on five layer PVDF films sandwiched by Al metal electrodes [14]. To measure the electronic transport properties in this 11-nm-thick PVDF film, an electrical contact on top-electrode pads was made using an AFM conductive tip and the W electrode was grounded. As shown in Fig. 2 (left), the current shows a dramatic decrease at both the positive (when sweeping the voltage from −4.5 V to +4.5 V) and the negative coercive voltages (when sweeping the voltage from +4.5 V to −4.5 V), while no current is detected in the low voltage region because of the instrument limitation.

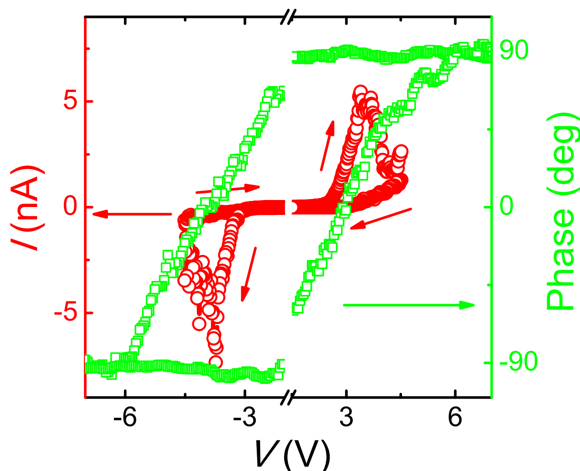

FIG. 2. (Color online) *I-V* curves in the device with 11-nm-thick PVDF film at a frequency of 0.5 Hz (left) and the out-of-plane PFM phase hysteresis loop (right).

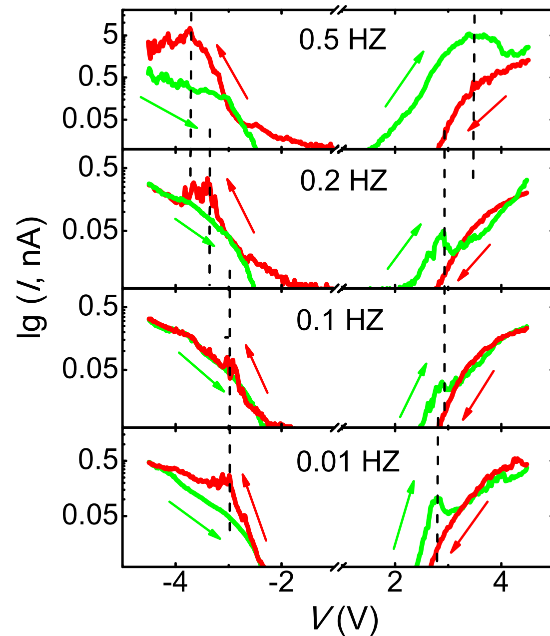

FIG. 3. (Color online) *I-V* curves in a nanodevice at frequencies of 0.01, 0.1, 0.2, and 0.5 Hz, respectively. The dashed vertical lines are a guide to the eyes showing the position of the current's jump corresponding to the coercive voltages.

The dramatic change in currents at the coercive voltage was usually attributed to the displacement current due to the polarization switching [19]. However, the integration of the current density produces a charge density of $\sim$0.1 C/cm^2, which represents an equivalent polarization which is about five orders of magnitude larger than that ($\sim$1 μC/cm^2) in PVDF thin films. The current is stable in each device and the value of the current varies slightly from one device to the other. Further analysis (not shown here) shows that the mechanism responsible for the observed current properties is dominated by a thermionic injection process, rather than a direct tunneling given the thickness of the studied film. Interestingly, the current curve indicates a resistive switching associated with polarization reversal occurs in this ultrathin ferroelectric film. Indeed, when the thickness downscales to a few nanometers (less than 20 nm), such kind of resistive switching by polarization reversal exists in organic ferroelectric films [20].

Figure 3 shows several *I-V* curves depending on the frequency (f) used for the sweeping voltage in this 11 nm-thick PVDF film. The logarithm of the current is intentionally plotted in Fig. 3 for a better determination of the position of the current's jump corresponding to the coercive voltage (as indicated by the dashed vertical lines in Fig. 3). It is worth mentioning that because of the limit of detection in our experiment (~0.03–0.04 nA), we cannot access the current at low voltages and that the sudden detection of the current is much more pronounced at lower frequencies. Note also that the amplitude of the current value might be affected by some local breakdowns reducing the effective area of electron injection. However, the value of the coercive voltage remains unaffected. Therefore, the measurements reported in Fig. 3

show that the coercive voltage unambiguously decreases by reducing the frequency f. Note that the coercive voltage tends to vary much less, if at all, when f is as low as 0.01 Hz.

We can now use the relationship between the coercive field E_C and f to analyze the polarization switching kinetics in this 11-nm-thick PVDF film [21,22]. Indeed, as mentioned above, intrinsic/homogeneous and extrinsic switching can be distinguished by their switching kinetics. In the homogeneous mechanism, the dependence of the switching rate τ^{-1} on the applied electric field near E_0 (intrinsic threshold coercive field) has the following form [8]:

$$f \sim \tau^{-1} \sim \beta(T) \left[\frac{E}{E_0} - 1 \right]^{1/2}, \tag{1}$$

where $\beta(T)$ is a constant at a given temperature. According to Eq. (1), there is thus a well-defined threshold field allowing the switching to happen. Moreover in the extrinsic case, the switching rate τ^{-1} has an exponential dependence on the reciprocal electric field E as follows [1,5,23–25]:

$$f \sim \tau^{-1} \sim C \exp\left[-\frac{\alpha}{E} \right], \tag{2}$$

where typically the activation field α has a reciprocal dependence on the temperature and the prefactor C is only very weakly dependent on E and T. In contrast to homogeneous switching kinetics, there is no threshold coercive field in this (nucleation and domain growth associated) extrinsic switching mechanism. Note that E in both Eqs. (1) and (2) is the electric field applied to the ferroelectric film when the polarization switches and thus it corresponds to the coercive field E_C in this experiment [21,22,26,27].

Figure 4 shows the dependence of the coercive electric field E_C as a function of the frequency f from three different devices. The red solid line and green dashed line are fits using Eqs. (1) and (2) with $E = E_C$, respectively. Unambiguously, Fig. 4 demonstrates that a homogeneous polarization switching mechanism takes place in the 11-nm-thick PVDF film.

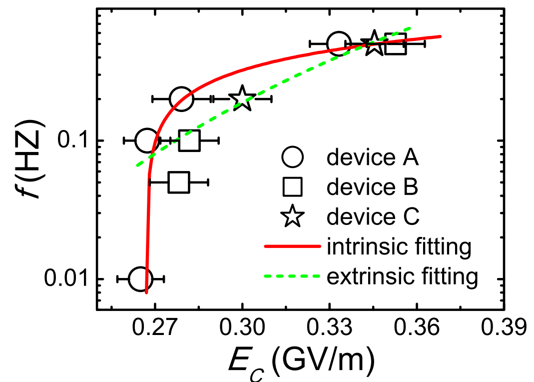

FIG. 4. (Color online) Coercive electric field E_C as a function of the frequency f from three different devices. The red solid line and green dashed line are fits to Eqs. (1) and (2), respectively.

Indeed, a critical behavior with a threshold field E_0 of about 0.26 GV/m is observed attesting the polarization switching is homogeneous. This value of E_0 is in good agreement with that of 0.35 ± 0.1 GV/m obtained in P(VDF-TrFE 70:30) copolymer LB films [7].

In summary, the polarization switching kinetics in 11-nm-thick pure PVDF ferroelectric film was investigated by *I-V* method. In agreement with LG theory, a critical behavior with well-defined threshold field was observed. This result demonstrates that a homogenous intrinsic switching occurs in this ultrathin homopolymer film, which further supports that such mechanism could be a general property of ultrathin ferroelectric materials.

This work was supported by the Major State Basic Research Development Program (Grant No. 2013CB922302), the Natural Science Foundation of China (Grants No. 11374320 and No. 11104301), and Natural Science Foundation of Shanghai (13JC1406000 and 14JC1406500). B.B.T., Y.L., X.F.B., and B.D. would also wish to acknowledge the China Scholarship Council (CSC).

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