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Study of the morphology of organic ferroelectric diodes with combined scanning force and scanning transmission X-ray microscopy

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ABSTRACT

Organic ferroelectric diodes attract increasing interest as they combine non-destructive data read-out and low cost fabrication, two requirements in the development of novel non-volatile memory elements. The macroscopic electrical characteristics and performances of such devices strongly depend on their structural properties. Various studies of their global microscopic morphology have already been reported. Here, a multi-technique approach including different scanning force and X-ray microscopies permitted to reveal and locally study nanometer-scale unexpected sub-structures within a P(VDF-TrFE):F8BT ferroelectric diode. The strong impact of these structures on the local polarizability of the ferroelectric is shown. Two alternative fabrication methods are proposed that prevent the formation of these structures and demonstrate improved macroscopic device performances such as endurance and ON/OFF ratio.

1. Introduction

Organic ferroelectric resistive switches can be used as nonvolatile memory elements in low-cost organic electronic circuits [1,2]. They usually consist of a phase-separated blend of ferroelectric and semiconductor polymers sandwiched between two metallic electrodes, combining key properties of the ferroelectrics (non-volatile data storage) and the semiconductor (conductivity/rectification). The resistivity of such diodes can be switched between two or more distinct levels via the control of the stray field emanating from the ferroelectric [3,4]. These levels retain their state even when the power is turned off. Hence, two-terminal non-volatile memory with non-destructive data read-out can be achieved and up-scaled by using simple crossbar array geometries [5,6].

Macroscopic electrical characteristics of such diodes have been reported [2,5,6]. However, it was also shown that the performance of ferroelectric diodes can significantly vary depending on the morphology of the phase-separated blend at the nanoscale, for example arising from different processing conditions [7,8]. The global morphology of such blend films was investigated [8–13], and was shown to consist of semiconducting circular vertical pillar domains embedded in a homogeneous ferroelectric matrix. Some semiconductor domains were found to percolate through the whole matrix layer from bottom substrate to top of the film, enabling proper subsequent electrical contact on both sides. Others semiconductor domains were found to be buried (not reaching the top film surface) or floating (not reaching the bottom substrate). Very recently, additional undesired nanometer-scale structures (called ”wetting layer”) between bottom contact and a P(VDF-TrFE):F8BT blend have been revealed by selective chemical dissolution [8,12]. This shows that the film growth processes are not fully under control at lower scale, which can severely impact on the electrical properties and also on the final diodes performance.

Here, a multi-techniques study of a P(VDF-TrFE):F8BT blend is performed to locally investigate at the nanoscale these structures and their influence on the device properties. Local surface and bulk morphological and electrical properties are investigated by a combination of Scanning Transmission X-ray Microscopy (STXM) and Scanning Force Microscopies (SFM), including Kelvin Probe Force Microscopy (KPFM) and Piezo Force Microscopy (PFM). This permitted to determine the nature and understand the origin of these structures.

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Further, these structures are demonstrated to have a detrimental effect on the local polarizability of the P(VDF-TrFE). Two alternative sample designs are proposed that suppress their formation. This results in a restored homogeneous polarization of the ferroelectric matrix and improved device performances via the increase of endurance and ON/OFF ratio.

2. Materials and methods

The active film of the ferroelectric diodes studied here consists of a 1:9 wt/wt blend of poly(9,9-di-*n*-octylfluorene-*alt*-benzothiadiazole) - F8BT, and Poly(vinylidene fluoride-trifluoroethylene) - P(VDF-TrFE), with 77 mol% VDF. Whereas the ferroelectric material P(VDF-TrFE) was supplied by Solvay Specialty Polymers, the semi-conductor F8BT was synthesized according to a modified Suzuki-polymerization [14,15]. The blend was spin-coated on metal-coated Si_3N_4 membranes (for the combined X-ray/AFM measurements) and glass substrates previously coated/patterned with a metal electrode (for all other measurements), and subsequently annealed at 50 °C or 135 °C for 1/2 to 1 h. The films obtained by this procedure exhibited a thickness of typically 200 nm. For the (patterned) bottom electrode Au, OH-passivated Au and MoO_x/Mo were used. The Au and Mo contact were obtained by evaporation, followed by the formation of a ≈1 nm oxide in the case of Mo. The OH- Au passivation was performed by a subsequent overnight immersion into a solution of 11-mercapto-1-undecanol. The top contact consisted of the SFM tip for all local measurements. For the electrical measurements, a barium electrode capped with aluminium was evaporated on the top of the film.

A schematics of the working principle of the ferroelectric diode is shown in Fig. 1. Since P(VDF-TrFE) is insulating, the current can only flow through the F8BT semiconducting domains. However, an ohmic contact to the electrodes is needed to inject charges. The bottom electrode material was purposely chosen to form a Schottky barrier at the interface with F8BT, insuring a limited charge injection and a low current flow. When the ferroelectric is polarized along the direction of the probing bias (Fig. 1A), the emanating stray field increases the apparent injection barrier and fully suppresses the current in the diode (OFF-state). In contrast, when the ferroelectric is inverse-polarized with respect to the probing bias (Fig. 1B), the stray field (curved dashed black arrows) lowers the apparent injection barrier at the semiconductor/metal interface and a higher diode current is observed (ON-state) [2,3]. The typical hysteretic loop between ON- and OFF-state of the diode is shown in Fig. 1C, with V_c being the minimum voltage to inverse-polarize the ferroelectric (coercive voltage).

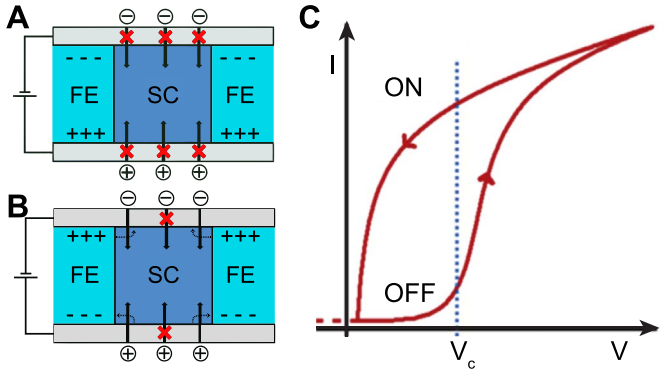

Fig. 1. A./B. Cross-sectional schematics of the diode, with the ferroelectric (FE, cyan) and the semiconductor (SC, blue) domains, top and bottom electrodes (grey), in the OFF-state (polarization and bias voltage with same polarity) and ON-state (polarization and bias voltage with inverse polarity), respectively. Polarization charges in the ferroelectric, direction of the stray field (black dashed arrows) and charge carriers transport in the semiconductor (black arrows) are indicated. **C.** Typical IV characteristics of an Au/P(VDF-TrFE):F8BT/Au diode, being switched in the ON-/OFF-state by applying bias with amplitude exceeding the coercive voltage V_c of P(VDF-TrFE). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Kelvin force microscopy was carried out on a prototype SFM instrument developed by Empa. Measurements were performed in ultra high vacuum at ≈ 10^{-8} mBar, with a Pt-coated tip from Nanosensors (PPP-ContPt). A phase-locked loop was used to drive the cantilever on its resonance of 12.9 kHz with an oscillation amplitude kept constant. To measure the Kelvin signal an oscillatory bias of 100 mV with a frequency of 9.7 kHz was applied, and the resulting oscillatory cantilever deflection was detected with a lock-in amplifier and minimised by adding a DC voltage compensating exactly the local surface potential. Note that since the surface potential originates from the electronic properties of material extending over several hundreds of nanometers in the depth, the full polymer film thickness is expected to contribute to the KPFM signal.

The combined X-ray/AFM data was measured at the NanoXAS beam-line of the Swiss synchrotron (SLS), Paul Scherrer Institute [16]. Measurements were performed in ultra high vacuum at ≈ 10^{-9} mBar. X-ray data were acquired in transmission mode at energy much higher than the carbon resonance (1 keV). The STXM data presented here show the absorbed X-ray intensity (I_0-$I_{transmitted}$), such that dark reflects low absorption and bright strong absorption. Thus, the STXM intensity predominantly reflects the film density and thickness. The topography was measured by AFM operated in contact mode with a Pt-coated cantilever from Nanosensors (PPP-ContSCPt).

The poling of the P(VDF-TrFE) matrix and piezo force microscopy study was achieved with a hrMFM instrument (NanoScan) at Empa. Poling and measurements were performed in contact mode operated in air. A Ti/Ir-coated AFM tip from Asylum Research (ASYELEC) with a contact resonance of ≈300 kHz was used to map the topography, pole the ferroelectric matrix by scanning it in contact with the blend [17] with a DC bias of ± 20/25V - well above the coercive voltage of the ≈ 200 nm-thick P(VDF-TrFE) films (≈ 10 V according to measured piezoresponse loops [18]), and to measure the PFM phase and amplitude maps. For the latter a lock-in amplifier from Zürich Instruments was used.

3. Results and discussion

3.1. Nature of the undesired structures

A typical P(VDF-TrFE):F8BT blend formed on Au substrate has been investigated by a combination of AFM and KPFM. Fig. 2A shows the topography of the blend, acquired by AFM operated in non-contact mode. One can distinguish the F8BT semiconducting circular domains within the P(VDF-TrFE) ferroelectric matrix, as already reported in previous work on this blend [8,12]. However here, all F8BT domains appear to protrude from the matrix surface. Moreover, additional unexpected structures, mostly visible as "cressant-like halos" surrounding the F8BT domains, are visible. Various effects can lead to this observation. Additional material of either types might have accumulated at the F8BT/P(VDF-TrFE) interface due to surface tension or capillary forces. On the other hand, because P(VDF-TrFE) is insulating, a charge accumulation might have occurred at the interface, leading to increased electrostatic force around the F8BT domains that in turn appears brighter. To elucidate this, KPFM measurements were performed on the same area with a locally compensated contact potential. Note that in contrast to conductive AFM (c-AFM) - where only fully percolating structures/domains can be detected via the measurement of the current flowing through them, KPFM probes the electrostatic interaction between tip and sample, that typically spans over several hundreds of nanometers (≈ $1/d^2$). Hence, electrostatic contribution from the whole film thickness - including local charges, even if very localized, is expected to be detected.

Fig. 2B and C presents the corresponding topography - this time free of possible charge effects, and contact potential maps, respectively.