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High-sensitivity piezoresponse force microscopy studies of single polyvinylidene fluoride nanofibers

Xia Liu, Xuanlin Kuang, Sixing Xu, Xiaohong Wang *

Institute of Microelectronics, Tsinghua University, Beijing 100084, PR China
Tsinghua National Laboratory for Information Science and Technology, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

We report piezoresponse force microscopy (PFM) studies of single electrospun polyvinylidene fluoride (PVDF) nanofibers on the Pt/Ti electrode substrate. The out-of-plane piezoelectric response is much stronger than the in-plane, which is dependent on the parameters of the electrospinning technique. Further, the local polarization switching of the thin nanofibers can be quantitatively characterized by the amplitude-voltage butterfly loop and phase-voltage hysteresis loop. The piezoelectric coefficient (d_{33}) of the nanofibers is diameter-dependent. The thinnest nanofiber studied here is 30 nm and has the maximal $|d_{33}|$ of 38.5 pm V^{-1}. The excellent piezoelectric properties of these low-dimensional nanofibers can facilitate the development in sensing and energy harvesting applications.

1. Introduction

Piezoresponse force microscopy (PFM) opens up a novel perspective on exploring the piezoelectric properties of the piezoelectric materials at nanoscale level [1]. Its popularity is due to the fact that the PFM provides direct experimental evidences on the interplay between the domain switching kinetics and microstructural features. Particularly, the PFM allows for the well-justified interpretation of the electromechanical coupling underlying many micro-/nanostructures [2], yet it is still a challenging issue when the PFM technique is applied to single electrospun nanofibers. First, it is difficult to fix the individual nanofiber on a conductive substrate. Second, the resolution is limited by the size of a PFM tip if the fiber diameter is less than 50 nm because of the thermal drift of the PFM system. In a typical PFM measurement, as we know, the tip applied with a voltage bias is brought into contact with the surface of a sample, and the tip deflection is induced from the expansion and contraction of the sample. The amplitude of the out-of-plane (OP) reflection is defined as the piezoelectric coefficient (d_{33}) of the material, and the phase describes its piezoelectric polarity. This method is suggested as an ideal tool for probing local piezoelectric properties. In fact, no other techniques are capable of probing directly the spontaneous polarization switching at nanoscale level [3].

Polyvinylidene fluoride (PVDF) and its copolymers exhibit piezoelectric, ferroelectric, pyroelectric, and electro-cooling effects. Moreover, owing to its polymeric nature, PVDF is more flexible, and lightweight and processable than conventional piezoelectric ceramics. Therefore, the piezoelectricity of the polymeric materials has attracted considerable interest in their applications in implantable biosensors and wearable and portable electronic devices [4,5]. Recently, the piezoelectric response imaging of some polymeric films or fibers was realized, but the further quantitative analysis of the thinner nanofibers such as piezoelectric switching behavior and d_{33} is seldom [2].

In this work, a series of PVDF nanofibers were prepared on the Pt/Ti/SiO_2/Si substrate by a far-field electrospinning technique. PFM was employed to study spatial imaging of piezoelectric switching and local piezoelectric response in the single nanofibers. Their diameter-dependent piezoelectric property was also studies. In addition to confirming the origin of their OP piezoelectricity, the PFM results reveal the details of stepwise amplitude and phase changes during the periodic polarization switching.

2. Experimental details

Electrospinning was performed on a SiO_2/Si substrate (bottom electrode) previously sputter coated with a Ti bottom layer and then a Pt top layer because the Pt has high surface energy. 16 wt

* Corresponding author at: Institute of Microelectronics, Tsinghua University, Beijing 100084, PR China.
E-mail address: wxh-ime@tsinghua.edu.cn (X. Wang).

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% PVDF ($M_w = \sim$534,000 g mol^{-1}, Sigma–Aldrich, USA) was dissolved in a solvent (4:6 DMAC and acetone) under stirring for 2 h at 60 °C [6]. The polymer solution was loaded into a plastic syringe (50 mL) fitted with a stainless steel needle (25G). A DC voltage of 30 kV was applied to the needle from a high voltage supply. The solution was injected into the needle at 1.0 mL h^{-1} using a syringe pump. Single as-electrospun nanofibers were collected on the conductive substrate placed at 12 cm from the needle tip.

PFM (Cypher S, Asylum Research) was employed to characterize the piezoelectric properties of the single PVDF nanofibers. In this method, a soft conductive cantilever with an Au/Cr coated tip (spring constant of 0.11 N m^{-1}, free air resonance frequency of 35 kHz) was brought into contact with the surface of the nanofiber. The tip was periodically biased and the responding deflections were translated into the mechanical motion of the tip. An AC bias (V_{ac}) riding on a DC bias was applied between the tip and the conductive substrate (Fig. 1). The vertical (out-of-plane, OP) and lateral (in-plane, IP) piezoelectric response imaging of the nanofibers was conducted using the dual AC resonance tracking mode [7]. The nanodomain switching behavior was then resolved quantitatively with a nanoscale resolution by switching spectroscopy PFM (SS-PFM) [8].

3. Results and discussion

With the AC bias applied between the PFM tip and the bottom electrode, the PFM allows for recording of the vertical piezoelectric

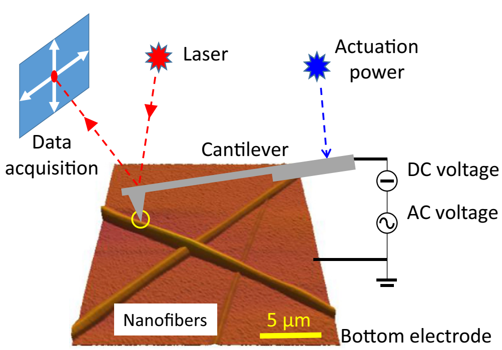

Fig. 1. Experimental setup for the measurement of the piezoelectric response of single nanofibers (the nanofibers in the figure is real).

response (VPR) and the lateral piezoelectric response (LPR) using the lock-in techniques [1]. The VPR reflects the cantilever vibrations in the vertical direction, while the LPR is described by the cantilever torsion in the length direction. Fig. 2 shows topography (a, b), VPR (c, d), and LPR (e, f) images (the so-called efficient piezoresponse signal) measured at the same nanofiber region in the resonant frequency mode (f_{ac} = 135 kHz, V_{ac} = 1.6 V). The PFM images show rather strong OP and weak IP piezoelectric responses. Hence, it can be inferred that the polarization direction of the dipoles lies at small angle to the direction perpendicular to the fiber axis and the bottom electrode. The VPR signals (Fig. 2c and d) show both positive and negative values suggesting the fact that the domains are mainly separated by 180° walls. In contrast, the LPR signals (Fig. 2e and f) are nearly unipolar. This verifies that the piezoelectricity of the PVDF nanofibers prepared by the far-field electrospinning is mainly derived from the OP electrical-to-mechanical conversion [9].

To determine their piezoelectric response in more details, the nanofibers were subjected to single point piezoresponse spectroscopy. The local piezoelectric response is detected as the tip deflection when the periodic bias ($V_{tip} = V_{dc} + V_{ac}\cos\varphi t$) is applied to the tip, as depicted by the schematic in Fig. 3a. The phase of the deflection, φ, yields the information on the polarization direction within the nanofiber. Therefore, hysteresis loops are captured in each point of the nanofiber and analyzed the coercive bias, polarization value, and polarization direction, providing a comprehensive interpretation of polarization switching behavior of the nanofiber. However, hysteretic effects in the PFM measurement may also arise from electrochemical and electrostatic effects [10]. In order to minimize the role of electrostatic effects, all the PFM measurements were conducted following the SS-PFM mode. In this method, the DC bias is applied in a train of pulses instead of sweeping continuously, while the phase and amplitude signals are read out at the "off-state" of the pulses as illustrated in Fig. 3a.

The real-time deflection (A) *versus* V_{dc} loop was measured by applying the DC voltage (from −30 V to +30 V) to the tip that was kept at a fixed position on the surface of the nanofiber (Fig. 3b). The maximal DC voltage was set beyond the coercive field of the nanofiber. Under the periodic applied DC voltage (top curve), the representative raw signals of the PFM measurement show the phase (middle curve) and amplitude (bottom curve) of the PVDF nanofiber (Fig. 3b). Correspondingly, the phase signal shows an around 180° switching in dipole moment when a positive voltage is applied. Every polarization switching happens in a period of

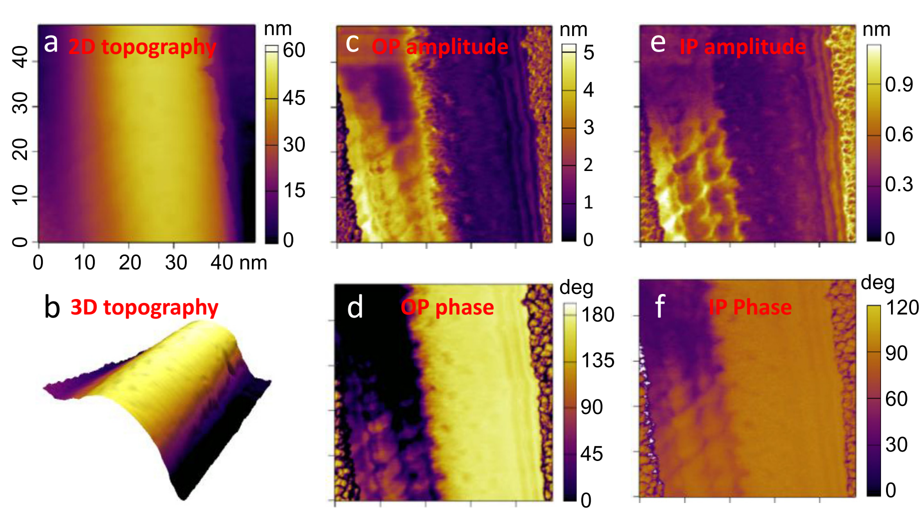

Fig. 2. (a, b) Topography images, (c, d) VPR images, and (e, f) LPR images of the single PVDF nanofiber.