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Full paper

Poling-free energy harvesters based on robust self-poled ferroelectric fibers

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ABSTRACT

Self-poling has been found in many two-dimensional epitaxial ferroelectric nanofilms originating from epitaxial growth clamping and has become a new research focus due to its potential applications in designing new types of ferroelectric devices. However, self-poling ferroelectrics based on internal strain gradients rather than external stimuli still do not exist. Here, we demonstrate a novel and unique design for one-dimensional structures and geometries in microscale with robust upward flexoelectric self-poling created by the application of electrospun ferroelectric fibers on a patterned substrate to introduce curving structure arises from the uneven substrate and confinement by other fibers in space. The fiber textile composed of these curving structures could resist external electric field and temperature, and can be fabricated into high performance poling-free flexible nanogenerators with outputs comparable to the poled ones. These results are conducive to providing a potential solution to the depolarization problem, to simplifying the technologies for manufacturing piezoelectric nanogenerators by avoiding the application of electric field for poling, and to providing extra freedom in controlling ferroelectric polarization and designing new types of devices.

1. Introduction

Ferroelectrics usually have different spontaneous polarization states originating from their noncentrosymmetric crystal structures below their Curie temperature as a requirement for lowering system energy, which can be aligned to exhibit macroscopic polarization through a poling process under an external electric field [1]. This macroscopic polarization is essential for their applications in piezoelectric nanogenerators and other devices. It is known that electrospun PVDF nanofibers may not require special poling process because both stretching and high electric field during electrospinning process could induce to form aligned ferroelectric β phase [2]. But for ceramic ferroelectric materials, in some situations it is difficult to pole some ferroelectrics when they simultaneously have a large coercive voltage and a low breakdown voltage, or the devices do not allow electrodes to apply an external electric field. Furthermore, the poled ferroelectric material may depolarize under external electric field and heating. If the spontaneous polarization orientation of ferroelectric materials is aligned at the time of material fabrication, and the self-poling is robust to resist external electric field and temperature, the techniques for constructing piezoelectric nanogenerators would be much simplified and improved [3] and it would be feasible to design new types of ferroelectric heterostructures and devices free from electrodes and the poling process [4].

The self-poling phenomenon has been found in many ferroelectric materials [3,4,6–10], and the overwhelming majority of these materials are two-dimensional (2D) epitaxial films. Various mechanisms have been proposed to explain the origin of self-poling, such as epitaxial clamping [3,4,10], charged vacancies [6], thermal strain, built-in electric field [7], etc. Another simple polarization control method is to impose external stress on the ferroelectric materials, similar to the application of an electric field. The changes in polarization in ferroelectric materials are strongly coupled with their deformation, leading to diversified electromechanical phenomena, including flexoelectric, electrostrictive, and piezoelectric effects [5]. Hence stress is an attempt to influence polarization based on the flexoelectric effect, which is defined as the generation of spontaneous electric polarization induced by a strain gradient [11]. For instance, the polarization state of epitaxial

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single-crystalline $BaTiO_3$ films can be mechanically switched by pushing an atomic force microscope (AFM) tip onto the surface [5]. The imprint of polarization can also be invoked by a strain gradient in uniaxial ferroelectric thin films [12] and by substrate bending of polycrystalline ferroelectric films [13]. It is obvious that it is necessary to apply an external force on the material in order to create flexoelectrically induced polarization. Therefore, a permanently self-poled ferroelectric that features polarization induced by the internal strain gradient without any type of external stimulus will be endowed with enormous advantages in terms of device fabrication and resisting depolarization caused by external field perturbations.

Here, we present a unique and effective approach to impose permanent aligned polarization on electrospun ferroelectric microfibers composed of typical ferroelectrics: barium zirconate titanate – barium calcium titanate (BZT-BCT) fibers, potassium sodium antimony-doped niobate ceramic – bismuth sodium potassium zirconate (KNNS-BNKZ) fibers, and lead zirconate titanate (PZT). Through the application of curving deformation in the ferroelectric fibers at the time of fabrication, the sample can change from having random polarization orientations to a stable strain gradient that induces robust upward self-poling derived from the flexoelectric effect without any poling process. These electrospun ferroelectric textiles with upward self-poling can be fabricated into high performance flexible nanogenerators (NGs) with outputs comparable to the poled ones, and show great potential for simplified and improved fabrication technique for piezoelectric devices.

2. Experimental section

2.1. Precursor solution preparation

The $0.5Ba(Z_{0.8}Ti_{0.2})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ precursor for electrospinning was prepared via a soft chemical method. Tetrabutyl titanate, barium hydroxide, calcium hydroxide, and zirconium acetylacetonate were added according to the stoichiometric ratio into a mixed solvent of ethanol, acetyl acetone, and acetic acid. Then, polyvinylpyrrolidone (PVP) was added under stirring to the precursor solution to adjust the viscosity, and the solution was then kept under stirring for more than 24 h in order to form a transparent precursor.

The $PbZr_{0.52}Ti_{0.4}O_3$ sol-gel precursor was prepared through adding tetrabutyl titanate, zirconium acetylacetonate, and lead subacetate into a mixed solvent of ethanol, acetyl acetone,and acetic acid according to the stoichiometric ratio, then adding PVP (Mr = 1,300,000) under stirring in order to form a transparent precursor with a suitable viscosity.

The preparation process for $0.96(K_{0.48}Na_{0.52})(Nb_{0.95}Sb_{0.05})O_3$-$0.04Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$ precursor was reported in our previous work [14].

2.2. Electrospinning process and nanogenerator fabrication

To prepare a sample for piezoelectric force microscopy (PFM) testing (Fig. 1(d)), a patterned substrate was prepared through sputtering Pt dot electrodes on a $Pt/Ti/SiO_2/Si$ wafer through a mask. The thickness of the dot electrodes was 400 nm, and the diameters of the dot electrodes were 100 μm and 1000 μm. After that, some BZT-BCT fibers were electrospun on it for 5 min, followed by calcination. Then, we conducted PFM testing in an edge region of the dot electrode.

To prepare the textile for NG fabrication, as shown in Fig. 1(a) and (b), the precursor was electrospun on an aluminum-foil-wrapped drum-type collector, at an injection rate of 0.015 mL/min under an electric field of 1 kV/cm for 4 h to obtain BZT-BCT textile. Then, the electrospun textile was peeled off from the aluminum foil after drying at 100 °C for 24 h, which was followed by a calcination process.

To fabricate the NG (Fig. 1(c)), the textile was cut into 1.5 cm × 1 cm rectangles, each of which put on a polyethylene terephthalate (PET) slice, and Cu conductive tapes were pasted on it as electrodes. To avoid any short-circuit connection between the two electrodes and to protect the ceramic textile, the structure was packaged with polydimethylsiloxane (PDMS) (premixed with curing agent in a ratio of 10:1 w/w) and cured at 80 °C for 24 h. To characterize the output of NGs under stable stress (Fig. 1(e)), a 300 g weight was released to free fall and strike the NG from a fixed height at a frequency of 0.275 Hz. The pressure was measured by a stress detector and could be controlled by changing the height. The NG was connected to a load resistance of 500 MΩ, and the output voltages across the load resistance were measured on an electrochemical workstation.

2.3. Characterization

The morphology and ferroelectric measurements were performed using a commercial atomic force microscope (AFM) with a piezoelectric force microscope (PFM) mode (Brucker Multimode 8). The ferroelectric phase angle versus tip bias loops were measured on the fiber surface as a function of a DC switching bias superimposed on an AC modulation bias.

3. Results and discussion

3.1. Self-poling design and examination

For ferroelectric materials, electrical polarization induced by a strain gradient based on permanent structures and geometries instead of the application of external stress [15,16] can be realized by the growth of the ferroelectric on a bumpy substrate. We electrospun some BZT-BCT fibers on a patterned substrate, and the as-prepared BZT-BCT fibers, which featured diameters of a few hundred nanometers, exhibited a polycrystalline perovskite structure, composed of many nanoparticles stacked together with dimensions of tens of nanometers as demonstrated in our previous work [17]. As shown in Fig. 2, BZT-BCT fiber were electrospun on a patterned substrate. It is obvious that, unlike the fiber lying on the flat region, the fiber lying on the dot electrode is curved on account of the convex electrode. Then, we conducted PFM in an edge region of the dot electrode. In the three-dimensional (3D) image of the sample, the edge of the dot electrode is clear, and the height variation along the blue line is about 100 nm. In the out-of-plane phase image (Fig. 2(a)), it can be observed that the fiber exhibits uniform upward self-polarization in its curving region. In the region away from the curving section, however, the fiber has more and more regions with downward polarization, and over its length, the fiber tends to display a random polarization orientation, reflected by the variation of phase signal, as well as the lower out-of-plane piezoelectric response compared to curving region (Fig. 2(b)). The contrast is more noticeable in Fig. 2(c) and (d), where we measured it in two regions inside the green boxes marked in Fig. 2(a). The fiber does not show any preferred in-plane polarization orientation or obvious in-plane piezoelectric response.

These results demonstrate that two distinct domain structures and polarization orientation states were successfully attained through the application of patterned substrate. If a fiber is electrospun on a patterned substrate, after calcination, the section on the dot electrode will be jacked up, and other section will lie flat on the substrate. As a result, the fiber becomes curved, with a strain gradient in the vertical orientation generated in the fiber. The centers of the negative and positive charges would mismatch thus creating a dipole along the direction of strain gradient, thus leading to a self-poling effect without any poling process. There would not be any strain gradient in the flat section of the fiber, so this region did not exhibit any preferred dipole orientation. The different electric polarization states of the two sections of the fiber could be fully explained by the different deformation states, so our design of one-dimensional ferroelectric structures and geometries to realize self-poling has been perfectly achieved.

The stabilization of the polarization by strong flexoelectric poling