

Fabrication and characterization of Ni/P(VDF-TrFE) nanoscaled coaxial cables

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The authors have prepared poly(vinylidene fluoride-trifluoroethylene) Ni/P(VDF-TrFE) nanoscaled coaxial cables with Ni nanowires as the cores and P(VDF-TrFE) nanotubes as the shells by a two-step process. Scanning electron microscope and x-ray diffraction measurements revealed the microstructure and crystallinity of the nanocables. Electrical measurements indicated that the nanocables possessed a large specific capacitance (~ 10.84 pC/mm²) and ferroelectric remnant polarization (~ 10 μ C/cm²) due to the composite structure. The distribution of electrical field in the nanostructure was also analyzed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2750391]

In recent years, the study of ferroelectric and piezoelectric nanostructures has attracted strong research interest due to the potential applications of these materials in nanoscaled sensors, actuators, and energy harvesting devices.^{1–6} Among many well-studied ferroelectric and piezoelectric materials, the poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer is a very unique candidate for nanodevices because it has a good sensitivity, high electromechanical properties, low dielectric constant, and low loss. It is a polymer so that its shape and size can be easily modified by conventional polymeric processing. Moreover, the ferroelectric and piezoelectric properties can be modified to a large extent by thermal treatment, irradiation, or by varying the molar ratio of PVDF and TrFE. While thin films and composites of P(VDF-TrFE) have been extensively studied in the past decades,^{7–13} recently there is an increasing interest to develop nanowires and nanotubes of this material.¹⁴ In the effort to fabricate sensors using such nanowires and nanotubes, we have encountered much difficulty in handling them mainly because P(VDF-TrFE) is soft and flexible. To solve this problem, we managed to introduce metallic nanowires in the P(VDF-TrFE) nanotubes aiming to provide additional mechanical support. In this letter we demonstrate one of such structures that we have recently developed—Ni/P(VDF-TrFE) nanoscaled coaxial cables in which Ni nanowires are the cores and P(VDF-TrFE) nanotubes are the shells. As to be demonstrated later in this letter, the introduction of Ni nanowires has led to significant enhancement in the dielectric and ferroelectric properties of the P(VDF-TrFE). The nanocable structure studied in this work consists of a functional organic material although many types of inorganic material-based nanocables have been reported in literature.^{15–21}

The nanocables were fabricated via a two-step process, as schematically shown in Fig. 1. Firstly, P(VDF-TrFE) nanotubes were fabricated by hot pressing using an alumina oxide (AAO) membrane as dual mould.¹⁴ The AAO membrane (Whatman, Anodisc, Ref. No. 6809 7023) is ~ 60 μ m thick and has through holes with a diameter of ~ 450 nm.

The P(VDF-TrFE) copolymer used in this work has a VDF/TrFE molar ratio of 70/30 and is known to possess good piezoelectric property. The hot pressing was conducted at 270 °C and with the application of a pressure of ~ 50 MPa for 15 min. By the capillary effect, P(VDF-TrFE) copolymer was squeezed into the template. After cooling to room temperature, P(VDF-TrFE) nanotubes were formed. Post-hot-pressing treatments were conducted. For example, the residual polymer on the major surfaces of the template was removed by using plasma etching, and a thin layer of gold was coated on one of the major surfaces by magnetron sputtering. Secondly, Ni nanowires were developed by cathodic electrodeposition using an electroplating system (Top Ward potentiostat with a dual-tracking dc power supply 6303D). This electroplating also led to the formation of a thin layer of Ni on the Au film. The quality of Ni nanowires was found to be very sensitive to processing conditions, including the electrolyte and its concentration, cathodic current, deposition time, and deposition temperature. Some of the as-deposited samples were further treated by soaking in a 4M sodium hydroxide (NaOH) solution to remove the AAO template, followed by cleaning in a de-ionized water bath.

The structure of the samples was characterized under a scanning electron microscopy (SEM). Figure 2(a) shows the top view of the sample after NaOH etching. It is observed that the tubes are round in shape with a diameter of ~ 450 nm and exhibit a roughly parallel arrangement. Ni nanowires are not observed in this figure because they are shorter than the P(VDF-TrFE) nanotubes. After the treatment in oxygen plasma, however, Ni nanowires can be clearly observed due to the partial removal of P(VDF-TrFE), as

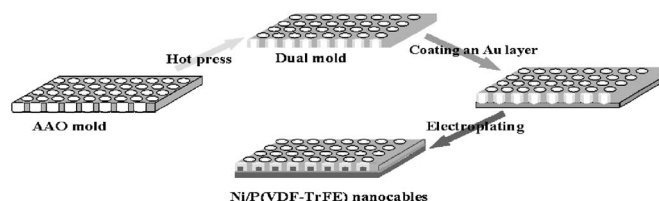


FIG. 1. Schematic process for the fabrication of Ni/P(VDF-TrFE) nanocables.

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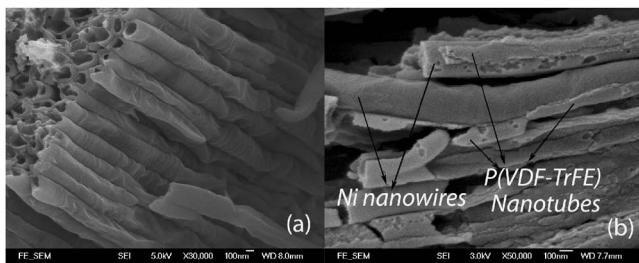


FIG. 2. SEM images of Ni/P(VDF-TrFE) nanocables: (a) Top view and (b) cross-sectional view.

shown in Fig. 2(b). The diameter of the Ni nanowire is ~ 250 nm.

The crystal structures of P(VDF-TrFE) and Ni in the samples were characterized by x-ray diffraction (XRD). Figure 3(a) shows the XRD measurement result. In the scanning range of 10° – 60° , three major peaks located at 19.6° , 44.4° , and 51.6° , respectively, are observed. The first peak was identified to represent P(VDF-TrFE), while the other two were found to belong to the Ni (111) and (200) reflections, respectively. The sharpness and intensity of the last two peaks indicate that Ni was well crystallized. To determine the crystallinity (X_c) of the P(VDF-TrFE) in the nanostructure, the first XRD peak ($13^\circ < 2\theta < 25^\circ$) was further analyzed. This peak is rather broad and asymmetric, suggesting that it is a combination of an amorphous and a crystallized phase of P(VDF-TrFE). Our data treatment was conducted first by removing the background noise and then by decomposing the remaining peak into two symmetric peaks using Gaussian and least-squares fitting. As shown in Fig. 3(b), two symmetric peaks were obtained, one located at 18.2° and another at 19.5° , which represent the amorphous and crystalline phases of P(VDF-TrFE), respectively. In general, X_c is defined by the formula $X_c = A_{\text{cry}} / (A_{\text{cry}} + A_{\text{am}})$, where A_{cry} is the area under the crystalline peak and A_{am} is the area under the amorphous peak.²² By calculation we found that $X_c = 60\%$. This value suggests that the P(VDF-TrFE) sample has a good crystallinity.

Dielectric and ferroelectric properties of the P(VDF-TrFE) in the nanocables were determined. The capacitance of the sample was measured using an impedance analyzer (Agilent 4294A) at 1 kHz. The nominal specific capacitance (defined as capacitance over electrode area) of the sample was found to be ~ 10.8 pF/mm². This value is about five times larger than the specific capacitance (~ 1.9 pF/mm²) of P(VDF-TrFE) thin films (50 μm thick, dielectric constant is 11) that we prepared and tested under the same conditions. The ferroelectric properties were determined by using a standard Sawyer-Tower circuit. As shown in Fig. 4, well-defined

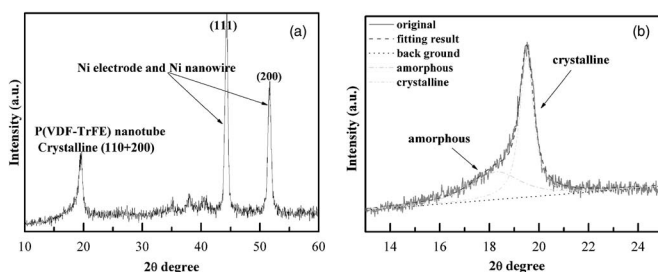


FIG. 3. (a) XRD pattern of P(VDF-TrFE) nanocables and (b) decomposing the first peak into two peaks.

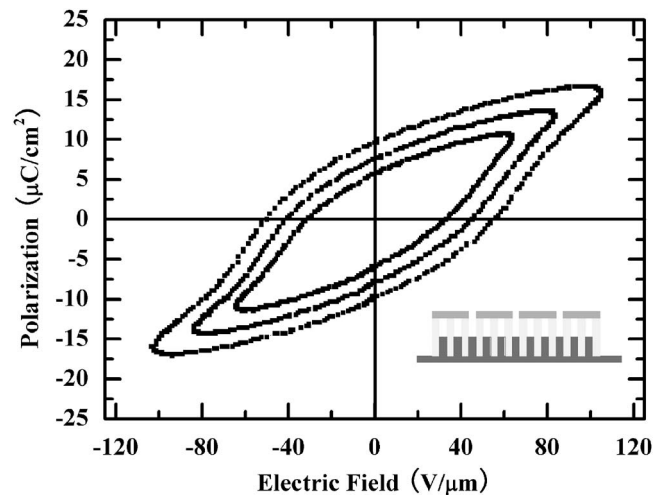


FIG. 4. Ferroelectric hysteresis loops of P(VDF-TrFE) in the nanocables (test frequency=10 Hz) and the structure schematic diagram of the nanocables.

ferroelectric hysteresis loops were obtained if the applied electric field is strong enough. Tested under a field with a maximum strength of 100 V/ μm , for example, the sample was found to exhibit a saturated hysteresis loop with a remnant polarization (P_r) of ~ 10 $\mu\text{C}/\text{cm}^2$ and coercive field (E_c) of ~ 50 V/ μm . This remnant polarization is three times larger than that of P(VDF-TrFE) thin films (~ 3.1 $\mu\text{C}/\text{cm}^2$).⁸

The enhancement of the dielectric and ferroelectric properties of P(VDF-TrFE) in the samples could be roughly explained as a result of the increase of the contact area between the metal and the polymer due to the existence of the Ni nanowires. To fully understand the ferroelectric behavior of the nanocables, it is also important to analyze the distribution of electrical field inside the dielectrics. We have conducted a calculation to simulate such distribution and the result is schematically shown in Fig. 5. The electric potential contours and electric field line distribution in the nanocoaxial cables were simulated by the finite element modeling using the commercial program ANSYS. Because of the periodicity of the nanocoaxial cables, only four metal nanowires were involved in the two-dimensional simulation. Quite obviously, the direction and strength of electrical field are dependent on location: (i) around the ends of Ni nanowires the electrical field is very strong, (ii) in the air columns on top of Ni nanowires the electric field is even stronger, and (iii) in

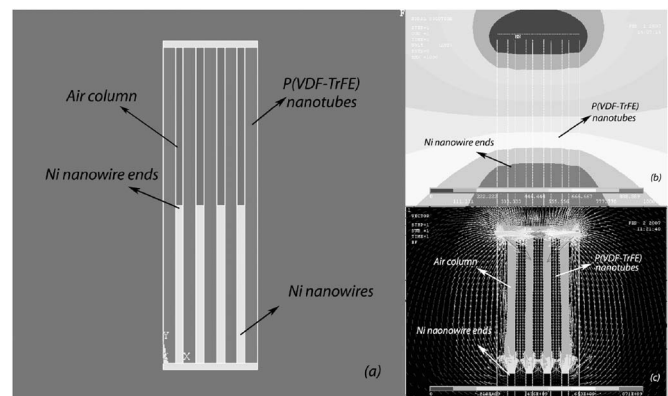


FIG. 5. (a) Schematic diagram of the nanocables, (b) distribution of potential contours, and (c) electric field in a nanocable under an electric field.

P(VDF-TrFE) nanotubes the field is weaker and the strength decreases as the site gets farther away from Ni ends. Due to the nonuniform distribution of the electrical field, the ferroelectric polarization in P(VDF-TrFE) is also strongly location sensitive. It is reasonable to assume that under an external field, the polarization around the Ni ends should be larger than the polarization in other sites. When the field is strong enough, the polarizations in the P(VDF-TrFE) around Ni ends will get saturated before the other sites. The overall result is that the ferroelectric hysteresis loop is quite tilted but the remnant polarization is enhanced if compared with P(VDF-TrFE) thin films.

In summary, we have prepared Ni/P(VDF-TrFE) nanoscaled coaxial cables by a two-step process and characterized the structure and properties. The introduction of Ni nanowires into P(VDF-TrFE) has significantly changed the dielectric and ferroelectric properties. Compared with conventional P(VDF-TrFE) thin films, our nanocables exhibited an improved dielectric property and enhanced ferroelectric polarization, suggesting that they may be useful for making some microsensors and microactuators.

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