Nylon-11 nanowires embedded in flexible substrates for piezoelectric transducers

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ABSTRACT

Nylon-11 nanowires have been fabricated in flexible track-etched polymer templates. Customized fabrication equipment was employed to realize an air-flow and gravity assisted template-wetting synthesis technique. X-ray diffraction analysis suggests that the strength of the piezoelectric phase of the nanowire crystals is directly proportional to the air-flow.

Keywords: piezoelectric, nanowires, flexible electronics, temperature stable, polymer, transducers, energy harvesters

1. INTRODUCTION

There is a critical need for cost-effective, flexible piezoelectric transducers that meet aerospace and military temperature specifications (−55 °C to 125 °C). Ceramic piezoelectric transducers are rigid and relatively expensive, and they typically contain heavy metals (such as lead) that are harmful to the environment. Polymer-based piezoelectric transducers are cost-effective and flexible but not as temperature stable. Thin-film polyvinylidene fluoride (PVDF) transducers have 80 °C maximum use temperatures[1] and are known to gradually lose their piezoelectric polarization with extended operation at temperatures near 60 °C.[2]

Previous research[2-4] has demonstrated that arrays of nylon-11 nanowires embedded in nanoporous anodic aluminum oxide (AAO) templates can be used to realize self-poling piezoelectric transducers that can operate at temperatures approaching 200 °C (the melting temperature of nylon-11) without losing polarization. In general, odd nylons (such as 7, 9 and 11) have strong hydrogen bonding and strongly aligned dipoles whereas even nylons (such as 6, 8 and 12) have alternating dipoles, which lead to net dipole cancellation[1,5]. The feature of self-poling in the nylon-11 nanowires, synthesized by means of template wetting, results from crystal alignment and polarization in the direction of the nanowire axis due to solvent tension in the nanopores prior to solidification. Nylon-11 nanofibers, with diameters that are comparable to those of the template-synthesized nanowires, have been synthesized via electrospinning[6]. However, electrospinning techniques typically produce nanofibers with randomized orientations. To maximize piezoelectric response, it is desirable for the nanostructures to have uniform orientation. Additionally, electro-spun nanofibers are not easily integrated into electrical circuity or sensor packaging.

This work describes a method for synthesizing nylon-11 nanowires in flexible nanoporous templates. The motivation is to realize flexible, self-poled transducers with improved temperature stability in comparison to current state-of-the-art flexible transducer technologies. Such devices include mechanical sensing as well as energy harvesting in a variety of vehicular applications.

2. SYNTHESIS METHODOLOGY

Fig. 1. depicts the process of a template- wetting technique for synthesizing nylon-11 nanowires in nanoporous polymer templates such as track-etched polyethylene (PETE) and track-etched polycarbonate (PCTE). Initially, 3- mm diameter, nylon-11 pellets (Sigma-Aldrich MKCK6155) were dissolved into heated formic acid for several hours. A 15 wt% solution was achieved by stirring 4.9459 grams of the nylon-11 pellets into a 125 mL Erlenmeyer flask containing 50 mL of formic acid (VWR Chemicals MFCD00003297). The pellets were added over a period of one hour. A magnetic stir bar was inserted into the flask, which was placed on a hot plate. The tip of a temperature probe was situated approximately one centimeter below the surface of the solution to ensure a constant temperature of 90 °C. The spin speed of the magnetic

stir bar was maintained at 400 revolutions per minute. Occasional agitation with a glass rod was used to break-up nylon-11 clumps. The flask was left on the hot plate (for approximately 12 hours) until the nylon pellets fully dissolved into the solvent and the solution became clear.

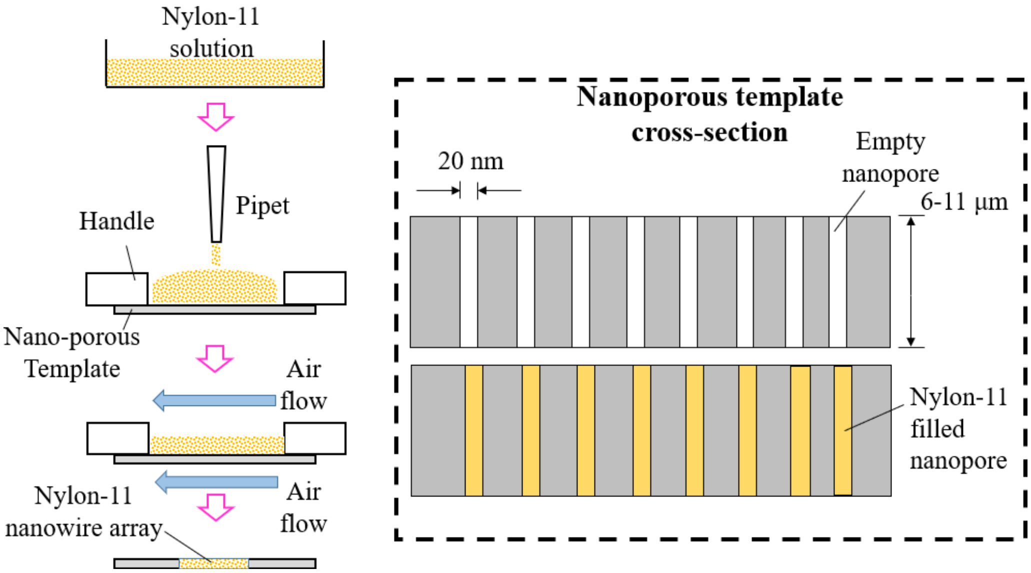

Figure 1. Nylon-11 nanowire flexible template synthesis process. Inset shows cross-sectional view of the templates filled and unfilled with our polymer mixture.

In this study, AAO and PETE templates with diameters of 25 mm and pore diameters of 200 nm were investigated. Because the nanoporous templates are non-rigid films with thickness ranging from 6 μm to 11 μm, they were adhered to rigid handles with polyimide tape to aid in material handling during the fabrication process. The handles were fabricated by milling 20 mm diameter holes in 30 mil thick polyvinyl chloride (PVC) sheets (i.e. blank credit cards). Using a pipet, a 150 μL ± 50 μL drop of nylon-11 solution was placed onto the top of a heated PVC sheet. The bottom of the taped template was then placed on top of the PVC sheet containing the solution. The entire assembly containing the template with the handles and the PVC sheet were taped together by the edges. The handle was then quickly transferred to a laminar flow chamber before the solution crystalized. Infiltration of the solution into the nanopores was due capillary action caused by the flow of air over the top of the material samples. It was important to note the handle was taped along the edges to aid the capillary action. The air flow was only being blown above the template to further pull the nylon solution upward through the nanopores. The handle assembly was left in the chamber for a duration of 15 minutes.

A laminar flow chamber, as illustrated in Fig. 2, was constructed for the purpose of maintaining a constant flow of air during the nanowire crystallization. Prior work[7,8] has shown that a piezoelectric δ' crystalline phase can be achieved by optimizing the air-flow speed over the sample during crystallization for a specific concentration of nylon-11 in the formic acid solution[4]. Our customized apparatus included a squirrel-cage blower attached to a collimator that was coupled to a clear PVC pipe. The collimator was constructed by tightly packing plastic drinking straws into a short section of PVC pipe. A variable transformer in conjunction with a handheld anemometer was used to control the speed of the laminar flow. Alignment markings inscribed on the clear PVC pipe were used to ensure that different samples were loaded in the same location of the chamber. The air-flow exiting the chamber was measured with a handheld anemometer before and after processing to verify process consistency.

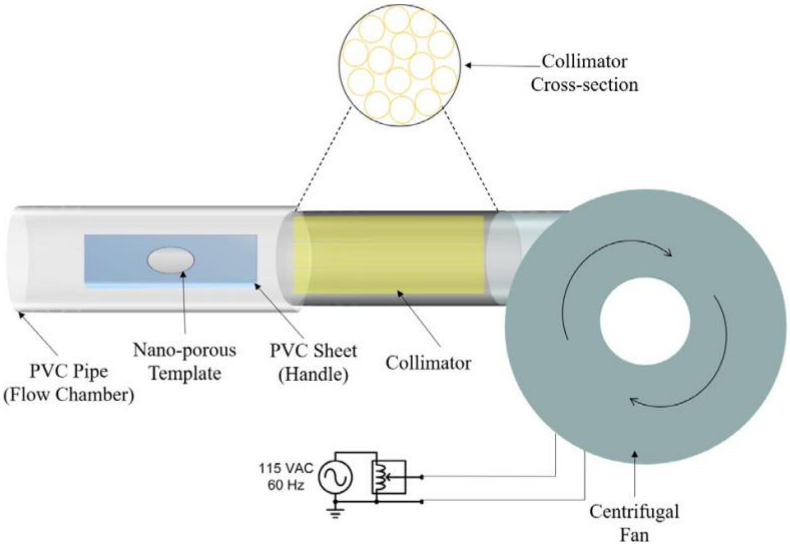

Figure 2. Laminar flow chamber for controlling piezoelectric phase and air-flow during nylon-11 nanowire crystallization.

3. CHARACTERIZATION

The nanowire formation and crystalline phase were verified using scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis, respectively. Fig. 3 shows a top-view SEM image of 200-nm diameter nylon-11 nanowires poking out of the flexible nanoporous template. The nanowires were formed using the air-flow assisted template-wetting technique.

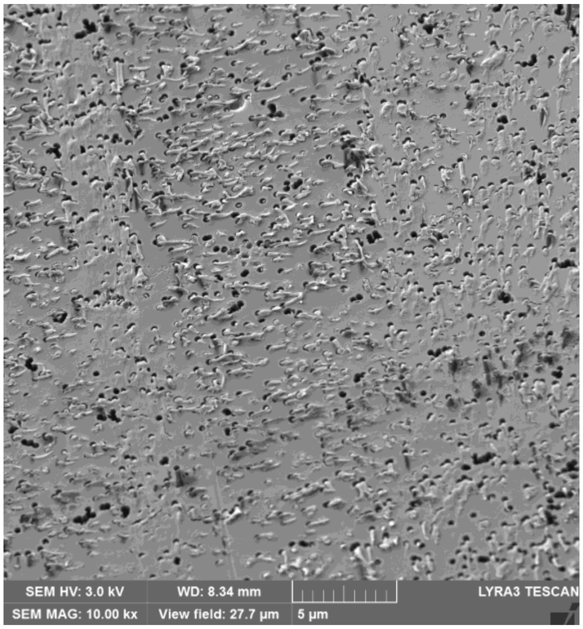

Figure 3. SEM image of the bottom of a flexible nanoporous polymer template. The nanowires are shown slightly poking out of the nanopores.

Fig. 4 shows the XRD traces pertaining to nylon-11 nanowires synthesized in PETE template assisted by air-flow speeds of 7.0 m/s, 9.0 m/s, and 11.0 m/s. To avoid altering the structure of the synthesized materials, the samples were measured *as-is* after processing. No effort was made to remove residual films left on the template surfaces (with chemical or mechanical treatments). Each trace shows 2θ peaks occurring in the vicinity of 20.15° and 21.6°. This peak signature corresponds to the δ' crystalline phase[9]. We observed that as the 2θ peak at 21.6° became more pronounced with an increase in air-flow speed.

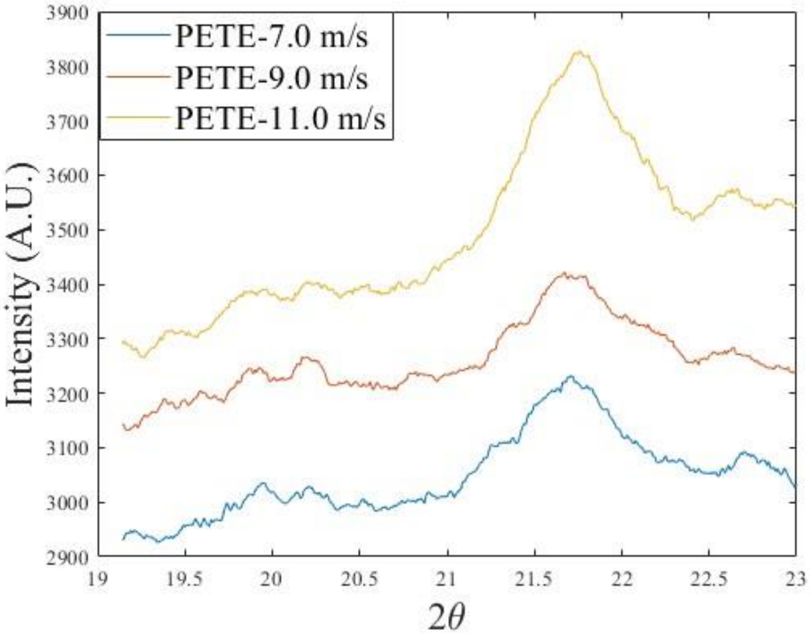

Figure 4. X-ray diffraction of a PETE template where the wind speed blown under the nanopores was 7.0, 9.0, and 11.0 m/s.

Because the nanoporous polymer templates produce strong XRD intensity backgrounds that coincides with the characteristic peak signature of the δ' crystalline phase, XRD was first performed on an unfilled nanoporous template. The trace from this measurement was subtracted from the traces produced by the nylon-11 nanowire samples. Additionally, noise in the traces were smoothed by a moving average with five points.

An electrical characterization of our nanowire filled templates was completed via a capacitance-voltage (CV) sweep. An AAO template had electrodes created using nickel conductive paint coating (MG Chemicals 841AR) on the top and bottom surfaces of the template. The capacitance was characterized as a function of direct current (DC) voltage bias. The template sample was connected to a probe station (Signatone 1160 Series Probe Station) which was used as the inputs to the characterization system (Keithley Semiconductor Characterization System Model 4200-SCS) responsible for the capacitance measurements. Fig. 5 shows the CV sweep using a DC voltage bias varying from -30 to +30 volts. Upon inspection of Fig. 5 a hysteresis loop can be noted which is electrically significant. The existence of the hysteresis loop from the AAO template filled with nylon-11 nanowire implies that the sample itself is exhibiting ferroelectric properties.

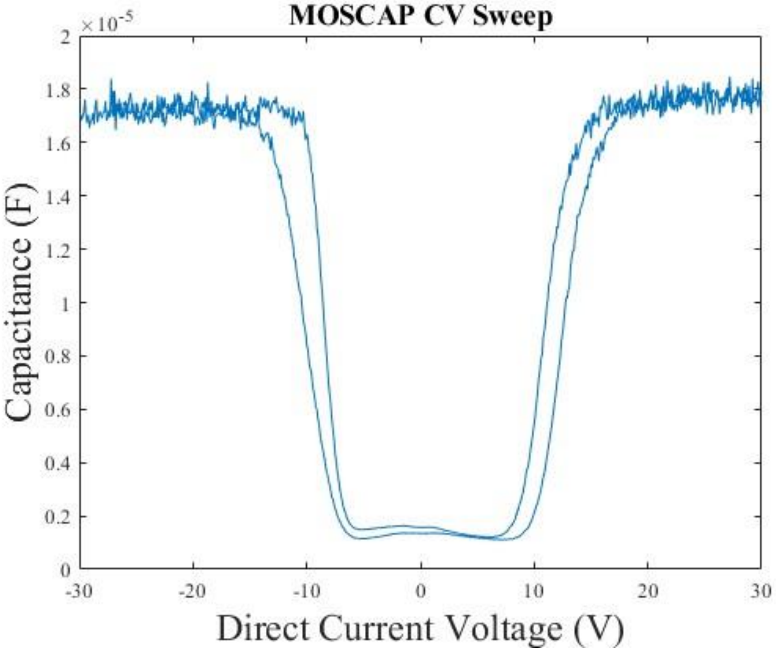

Figure 5. CV sweep for a rigid AAO template filled with nylon-11 nanowires.

4. SUMMARY

A technique has been developed for synthesizing nylon-11 nanowires in nanoporous templates. Nanowire synthesis was verified with SEM, XRD and CV characterizations. The nanomaterial synthesis is the first step towards enabling flexible piezoelectric transducers with improved temperature stability. Future work will include characterizing polymer-based templates nonlinear capacitance as a function of DC voltage bias and electrically measuring mechanically induced piezoelectric signals.

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