



Confinement effect on coercive field in relaxor terpolymer nanowires



B.L. Liu^{a,b}, B.B. Tian^{a,b,c}, J.L. Sun^{a,b,*}, Y. Liu^{c,**}, J.L. Wang^{a,b}, Sh. Sun^{a,b},
X.J. Meng^{a,b}, J.H. Chu^{a,b}

^a National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Yu Tian Road 500, Shanghai 200083, China

^b University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, China

^c Laboratoire Structures, Propriétés et Modélisation des Solides (SPMS), CentraleSupélec, UMR-CNRS 8580, Université Paris-Saclay, F-92290 Châtenay-Malabry, France

ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form 8 June 2015

Accepted 11 July 2015

Available online 16 July 2015

Keywords:

P(VDF-TrFE-CFE) nanowires

Confinement effect

Fourier transform infrared spectroscopy

ABSTRACT

The confinement effect on the coercive field in relaxor ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)[P(VDF-TrFE-CFE)] terpolymer nanowires with different diameters ranging from 30 to 170 nm was studied using piezoelectric force microscope. It was found that the coercive field increases significantly as the diameter of terpolymer nanowires decreases. The results can be explained by the conversion of molecule conformation from T_3G to $T_{m>4}$ in the terpolymer nanowires, which is supported by Fourier transform infrared spectroscopy.

© 2015 Published by Elsevier B.V.

1. Introduction

Arrays of polymer nanostructures have attracted much attention recently due to their potential applications in photonic, electronic, mechanical and biomedical devices [1–9]. In particular, one-dimensional (1D) nanostructures with a high aspect ratio (length/diameter) are appropriate for studying size-dependent processes with length scales comparable with the size of nanostructures, such as phase separation in block copolymers, or crystalline textures [10,11]. In addition, the size-dependent physical behaviors are of great importance and interest for both fundamental research and practical applications. The relaxor ferroelectric polymers, such as the electron irradiated poly(vinylidene fluoride/trifluoroethylene) [P(VDF-TrFE)] copolymer and poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] terpolymer exhibit outstanding dielectric and electromechanical properties because of their particular organic nanostructures [12–15]. It was reported that all-trans ($T_{m>4}$) polar conformations can be converted into shorter all-trans conformations by the irradiation induced defects and the dominant trans-gauche (T_3G) chain conformation is responsible for the

relaxor behavior [12,14,16]. The conformations may be sensitive to the size of the system and it is thus expected that the corresponding properties can be significantly modified as the scale approaches nanometer range because of the so-called confinement effect [17]. For instance, ultrathin Langmuir–Blodgett (LB) P(VDF-TrFE-CFE) film (less than 3.2 nm) demonstrates a ferroelectric-like feature [18]. Therefore, it is of great interest to investigate how the organic relaxor ferroelectrics behave as the nanowire size decreases.

In this study, the confinement effect on the coercive field in relaxor ferroelectric terpolymer P(VDF-TrFE-CFE) nanowires with diameters ranged from 30 to 170 nm was investigated by piezoelectric force microscope (PFM). As the diameter of nanowires decreases, reduced crystallinity and enhanced ferroelectricity in terpolymer nanowires were observed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR), respectively. The possible physical explanation is proposed to understand these interesting properties.

2. Experimental

Terpolymer nanowires of P(VDF-TrFE-CFE) (56.2/36.3/7.5 mol.%) (Piezotech, France) were fabricated by melt-wetting of the terpolymer in the anodized aluminum oxide (AAO) templates [19,20]. The process is presented in Fig. 1a. The AAO templates were cleaned with standard procedure and then kept at 400 °C for 4 h to remove impurities on surface of the nano-pores. The solution of 15 wt% P(VDF-TrFE-CFE) dissolved in butanone was

* Corresponding author at: University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, China.

** Corresponding author.

E-mail addresses: jlsun@mail.sitp.ac.cn (J.L. Sun), liuyangphy52@gmail.com (Y. Liu).

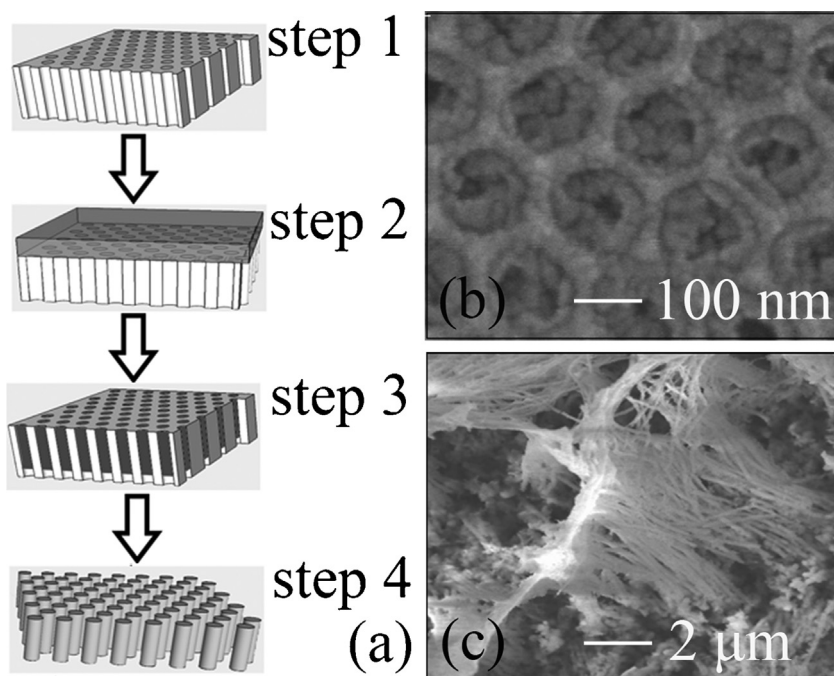


Fig. 1. SEM images of the P(VDF-TrFE-CFE) nanowires: (a) fabricating process; (b) P(VDF-TrFE-CFE) nanowires filled in the nanopores of the AAO templates; (c) the free standing nanowires.

dropped on top surface of the AAO templates and annealed at 60 °C for 30 min to volatilize butanone. To ensure full infiltration of the terpolymer into the nanopores of the templates, the samples were kept at 180 °C for 4 h in a vacuum oven. The SEM image in Fig. 1a shows the effectiveness of this procedure. Then the samples were cooled down to 118 °C and kept for 6 h for crystallization. The excess terpolymer on the top of the AAO templates was erased carefully using acetone. To remove the templates, the samples were immersed into a 4 M sodium hydroxide (NaOH) solution for 3 min and rinsed with distilled water. The freestanding terpolymer nanowires obtained is shown in Fig. 1b.

The morphology and local piezoelectric response of terpolymer nanowires on Pt coated Si substrates were measured by a commercial atomic force microscope (AFM, Bruker multimode 8) with a PFM module. The X-ray diffraction of the P(VDF-TrFE-CFE) nanowires in AAO templates was obtained with a highly accurate two-axis diffractometer in a Bragg–Brentano geometry using Cu K α wavelength with diffraction angles precision better than 0.002° (2 theta). A Nicolet 510 spectrometer with a 2 cm⁻¹ resolution and averaged over 16 scans was used to obtain the FTIR spectra to analyze the chain conformation in terpolymer nanowires.

3. Results and discussion

The diameters of the terpolymer nanowires were characterized by AFM topography. To be more specific, the diameters of terpolymer nanowires are ~30, 50, 120 and 170 nm, which are illustrated in Fig. 2a–d, respectively (note that the topography of 90-nm nanowire is not provided here). It is confirmed that the robust terpolymer nanowires with even diameters are obtained by our technique aforementioned.

The crystallinity in terpolymer nanowires with various diameters was checked by XRD. As a reference, the XRD of a thick terpolymer film was also obtained. The height of the (1 1 0, 2 0 0) peaks in the XRD curves for terpolymer nanowires decrease remarkably with the decrease of the diameter of the nanowires, as can be seen in Fig. 3, even though the volume fraction of

terpolymer nanowires does not differ significantly from each other. Obviously, the terpolymer nanowire with a relatively smaller size has lower crystallinity. This result is consistent with that reported in homopolymer poly(vinylidene fluoride) (PVDF) and copoly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] nanowires [21–24]. One possible reason may be due to the significantly reduced mobility of the macromolecular chains under confined geometry [17].

The coercive field of the terpolymer nanowires was extracted from PFM measurement. The hysteresis loops of piezoresponse amplitude and phase versus voltage for the terpolymer nanowires are shown in Fig. 4a and b, respectively. Curves within the yellow circle region are amplified in the left inset in Fig. 4b. The shifting of the hysteresis curve along the field axis may result from oriented polar defects in the nanowires [25]. The coercive field (E_C , derived from the lowest amplitude position) in terpolymer nanowires is shown in the right inset in Fig. 4b. Surprisingly, it is found that E_C increases significantly as the diameters of terpolymer nanowires decreases. Specially, E_C in the nanowire with its diameter of 30 nm is up to 18 MV/m, which is almost 4 times of that (~4.4 MV/m) in the nanowire with 170 nm in diameter. This result indicates that a polar conformation, which is hard to switch, may appear and extend its proportion in terpolymer nanowires as their size decreases.

In the PVDF based polymers, the all-trans $T_{m>4}$ conformation has the largest polarity while alternating trans-gauche $TGTC'$ conformation and combined T_3GT_3G' are less polar [26–29]. The shorter less-polar conformations T_3G and TG are abundant in terpolymer [12,14,18,28]. This results in the very small E_C in the thick terpolymer film and nanowire (diameter ~170 nm). As the size of terpolymer nanowires decreases, a conversion from T_3G conformation to $T_{m>4}$ conformation may occur. The $T_{m>4}$ conformation is difficult to be switched by an applied electric field, thus leads to a significantly enhanced E_C as shown in the right inset of Fig. 4b.

To confirm this explanation, the FTIR spectroscopy was performed in these nanowires since the infrared (IR) absorbance bands are very sensitive to the local chain environment. The absorbance spectra in the range from 450 cm⁻¹ to 1750 cm⁻¹ is presented in

Download English Version:

<https://daneshyari.com/en/article/5354384>

Download Persian Version:

<https://daneshyari.com/article/5354384>

[Daneshyari.com](https://daneshyari.com)