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Time-resolved fractal dimension analysis in ferroelectric copolymer thin films using R-based image processing

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ABSTRACT

We have developed time-resolved fractal dimension analysis in ferroelectric copolymer films in order to understand the effect of polarization relaxation on domain wall roughness. Interestingly, the progressive polarization relaxation of irregular domains results from the domain back reversal at the boundaries where the antiparallel polarization encounters, and therefore has a significant influence on the fractal dimension of the irregular domains as a function of time.

1. Introduction

Ferroelectric polymers have attracted significant interest for emerging applications, such as flexible memories, energy harvesters and electronic skins [1–6]. Among the numerous ferroelectric polymers, poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) are very notable not only for their relatively large remnant polarization values but also for their transparency and flexibility [7,8]. Recently, nanoscale phenomena in the P(VDF-TrFE) thin films have been explored by piezoresponse force microscopy (PFM) which probes bias-induced surface displacement and visualizes ferroelectric domain structures [9–12]. PFM allows us to understand polarization reversal mechanisms and domain wall dynamics at nanoscale. The progressive polarization loss in the ferroelectric polymer films has been studied in terms of switching dynamics or stability of written polarization states. However, its effect on domain shape and domain wall roughness has not been fully investigated.

Previously, we demonstrated that the fractal dimension analysis of irregular domains was very valuable for understanding the evolution of the domain geometry in the switching process [11]. An important issue in the aforementioned applications would be time-dependent change in ferroelectric properties. In this study, we report time-resolved fractal dimension analysis in the P(VDF-TrFE) thin films to understand the effect of polarization relaxation on domain wall roughness. We also suggest a new image processing algorithm based on the EBImage package in R to extract domain structural parameters, such as domain size and perimeter, for fractal dimension analysis and verify its efficacy on the time-dependent fractal dimension analysis with massive data.

2. Experimental

The detailed preparation of P(VDF-TrFE) films is described elsewhere [12]. Its microstructure was investigated by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). PFM measurements were performed using a commercial atomic force microscope (AFM, XE-120, Park Systems) equipped with a lock-in amplifier (SR830, Stanford Research System). An ac modulation voltage of 1 V_{rms} at 17 kHz was applied to a Pt/Ir-coated Si tip (PPP-CONTPt, Nanosensors, force constant $k \approx 0.2\ N\ m^{-1}$). A scan area of $5\ \mu m \times 5\ \mu m$ was switched as upwards at -7 V to the AFM tip and then a series of pulses with different positive voltage and pulse widths were applied to the tip in the background poling area to form downward dot domains. Subsequently, PFM amplitude and phase images were simultaneously taken by scanning $4.0\ \mu m \times 4.0\ \mu m$ with 512×512 pixels as a function of time. The relative humidity (RH) in the chamber was kept 40% during the PFM measurements. In the PFM amplitude images, the bright regions indicate domains with strong out-of-plane polarization orienting either downward or upward. The dark regions are mainly observed near the domain

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boundaries, where two opposite domains contribute equally to the tip vibration signal [12,13]. In the PFM phase images, the bright regions correspond to domains with upward polarization, whilst the dark regions represent domains with downward polarization. To determine fractal dimension of each domain, image processing was performed by using an EBImage package in R (R 3.3.1, GNU General Public License). R is a language and environment for statistical computing and graphics. The EBImage package is a toolbox of image processing and analysis for R. It features multi-dimensional image processing, a range of fast image processing, seamless integration with R's native array data structures and coherence of the user interface.

3. Results and discussion

In Fig. 1, the ferroelectric P(VDF-TrFE) film was uniformly fabricated on the platinized substrate and its thickness was 25 nm. In FTIR spectrum, ferroelectric polar β-phase was confirmed by the characteristic bands corresponding to *trans* sequences longer than TTTT (1290 cm^{-1}) and longer than TTT (1200 cm^{-1} and 889 cm^{-1}). In XRD, the prominent peak at $2\theta = 19.8°$ due to (1 1 0) and (2 0 0) reflections of the crystalline β-phase also was observed. Fig. 2 shows a schematic diagram of time-resolved fractal dimension analysis using our R-based algorithm. To obtain accurate area and perimeter of each written domain, a PFM phase image (i.e. a binary digital image) is converted into a three-column data containing horizontal position (X), vertical position (Y) and polarization direction (Z) of each pixel. It should be noted that a positive value indicates upward polarization and vice versa. Firstly, positive values in the Z column are assigned to 0 and negative ones are left unchanged. This is a 'domain isolation' step in our image processing, which separates a certain domain structure from the background and eliminate nuisance noise. Secondly, a new PFM phase image can be generated from the processed data and then the image is divided into 9 image tiles containing only single downward domain of interest. Thirdly, pixels of value 0 are considered as background (black) and other pixels are recognized as an object (grey) in the image tile for further analysis. The number of pixels corresponding to the object are obtained to calculate its perimeter (i.e. a path that surrounds a two-dimensional shape) and area. In this case, pixel length and area are 12.2 nm and 61 nm^2,

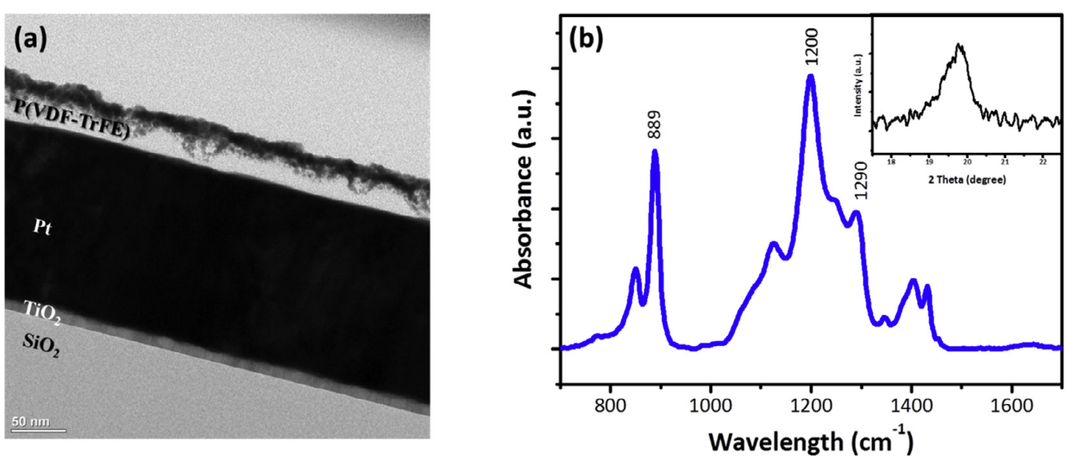

Fig. 1. (a) TEM cross-sectional image and (b) FTIR spectrum of the P(VDF-TrFE) film. The inset shows XRD patterns to determine its crystallinity.

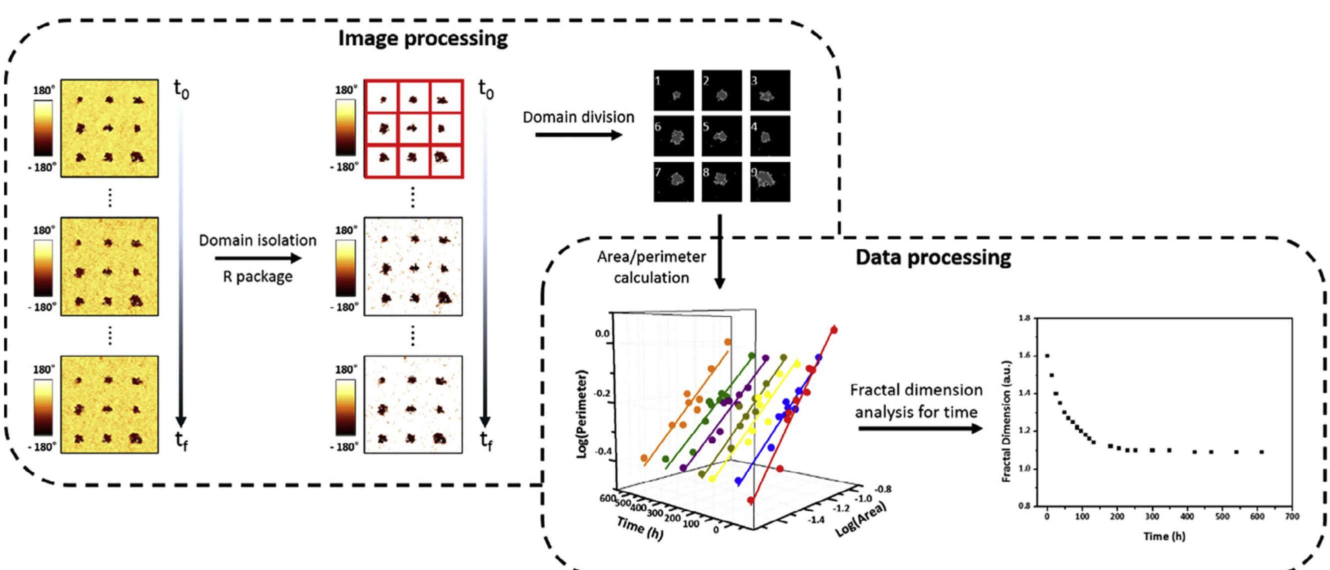

Fig. 2. A schematic diagram of time-resolved fractal analysis using PFM phase images.