Nanoinprint of ordered ferro/piezoelectric P(VDF-TrFE) nanostructures

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ABSTRACT

The next generation of portable computing and communication devices tremendously depend on the technologies that enable the rapid manipulation, caching and high-density non-volatile data storage. The recent development of organic electronics requires high-quality organic memory compatible with other devices, which will eventually lead to the realization of all organic electronic systems. The challenge of the organic electronics application is to find less degradative ways of fabricating ferroelectric polymer nanostructures. In this work, we applied the nanoimprint technique to fabricate ferroelectric poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer line and dot nanostructures and compared the ferroelectric properties and domain formation in these two nanostructures.

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1. Introduction

In recent years, poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] and its copolymers with trifluoroethylene have been extensively studied as an active medium for non-volatile data storage with promising memory characteristics such as large remanent polarization, good fatigue and retention properties [1]. For the increasing demand of the device miniaturization, most works focus on developing nanostructured ferroelectric patterns with smaller feature size, higher density and improved sensitivity [2]. However, the transition from low-density to high-density non-volatile memory without ferroelectric degradation requires a major breakthrough in the patterning technique [3]. For the traditional method, the ferroelectric materials are usually patterned by lift-off, focused ion beam, wet or dry etching processes which are generally complicated and expensive. The nanoimprint lithography (NIL), on the contrary, might be capable of a rapid, large-area and low-cost technology for the nanostructure formation with good crystallinity [4]. In the former reports, the majority studies focus on the structures imprinted while with little emphases on the functional properties [5]. Our previous work shows that NIL technology offers a low-cost and effective way to fabricate P(VDF-TrFE) nanoscale structures, and to simultaneously control the orientation and crystal quality in the patterned films [6]. In this work we utilize Piezoresponse Force Microscopy (PFM) to investigate the effects of the nanoimprint process on the ferroelectric and piezoelectric properties and to map the localized ferroelectric domain arrangements of the nanoimprinted P(VDF-TrFE) thin films.

2. Experiment

The P(VDF-TrFE) copolymer with a molar ratio of 70/30 was dissolved in methyl ethyl ketone (MEK) and spin-coated onto the substrates that were prepared by evaporating 5 nm Ti and 100 nm Pt on Si wafers to serve as the bottom electrode for the PFM measurements. The samples were then heated at 80 °C for 30 min and formed 300 nm P(VDF-TrFE) films. Nanoimprint was performing on the films thereafter as illustrated in Fig. 1a. Two types of gratings structures, a 2D square grating and 1D line grating templates, were used as imprinting molds to form the dot array and line patterns on the films, respectively. The 2D square grating Si template has a 500 nm diameter dot and 1 μm in period, and the 1D line grating template has a period of 1 μm, line width of 250 nm. The imprinting temperature and pressure are 135 °C and 1.6 N, respectively. The Atom Force Microscopy (AFM) has been used to investigate the structure of the P(VDF-TrFE) film and the PFM to study the piezoresponse at nanoscale after nanoimprinting process.

3. Results and discussion

Fig. 1b shows the 3D morphology of the nanoimprinted samples measured by AFM. The upper and lower images in Fig. 2 show the topography images and vertical PFM (VPFM) amplitude images, respectively, in unimprinted area (Fig. 2a), imprinted grating struc-
ture (Fig. 2b) and dot array structure (Fig. 2c). Striking ferroelectric ordering is observed in the imprinted areas following the periodic mould structures, whereas only random polarization appears in the unimprinted region. This can be clearly seen from the sectional profiles (Fig. 3) along the line scans in Fig. 2a and b, which reveals a piezoelectric contrast of as high as 2.6 mV in the imprinted region, while no piezoelectric contrast in the unimprinted area. Fig. 2b and c also indicates that the edges of imprinted patterns tend to have larger piezoelectric response than other regions and the most pronounced piezoresponse is located at the steeper edges of the nanostructures. The asymmetry in the topography of the imprinted samples is caused by slight uneven impress off the surface normal of the films during embossing process, which leads to different angles as well as possible different preferred crystalline orientation at both sidewalls. Hu and co-workers have observed that the PVDF crystal orientation is strongly affected by the thermomechanical history, especially at the interface between the template trench edge and molten polymer, experienced by the material during embossing [7]. The fact that the largest vertical piezoresponse occurs at the steeper sidewall suggests that polar b-axis is preferably oriented along the film normal at the sidewall. Such crystalline orientation arrangement after nanoimprint corresponds to the partial

![Diagram](image)

**Fig. 1.** (a) The schematic illustration of ferroelectric film P(VDF-TrFE) nanoimprint process. (b) 3D morphology images of samples with imprinted depth of 300 nm and 350 nm.

![Graphs](image)

**Fig. 2.** The upper and lower images show the topography images and vertical PFM (VPFM) amplitude images, respectively. (a) in unimprinted area, (b) in imprinted grating structure and (c) dot array structure.
confinement embossing condition of PVDF proposed in [7], where the template trench depth is much smaller than the film thickness.

To further illustrate the effects of nanoimprinted structures on the ferroelectric properties of P(VDF-TrFE) films, both the 3D and 2D VPFM amplitude images from the nanoimprinted line and array structures are shown in Fig. 4. The VPFM amplitude image provides information about the strength of the electromechanical coupling with each dot. External electrical field was also applied to the imprinted samples to study the ferroelectric switching behavior. After the nanoimprinting process, both positive and negative voltages of ±12 V were applied on an area of 2 × 2 μm². The 3D and 2D VPFM images after the switching writing are displayed in Figs. 4c and f. One can find that under such voltages, the trench area in the pattern can be rewritten by external positive or negative voltages, while the protruded dot array remained almost unchanged due to its larger thickness and thus higher switching voltage. Finally, we also measured the PFM phase and amplitude for the imprinted region as shown in Fig. 5a and b. The switch polarization phase is 180° and the piezoelectric coefficient $d_{33}$ is ~60 pm/V, compared

Fig. 3. Sectional profiles from VPFM amplitude images of imprinted and unimprinted areas in Fig. 2b and a respectively.

Fig. 4. 3D (a–c) and 2D (d–f) VPFM amplitude images from imprinted P(VDF-TrFE) film. In (c) and (f), a 2 × 2 μm² region in the center was rewritten with a DC tip bias of 12 and −12 V, respectively.

Fig. 5. (a) and (b): Hysteresis dependences of out-of-plane piezoresponse phase and piezoelectric coefficient, respectively, with applied voltage from −10 to 10 V in the imprinted region.
with the value of $d_{33}$ ranging from 3 to 19 pm/V at uniform films without imprinting in the previous work[5], indicating that the nanoimprint process retains excellent ferroelectric properties in the P (VDF-TrFE) films. We believe that it is attributed to the thermo mechanical effects during nanoimprint process when the print mould was pressed against the polymer film under pressure of 1.6 N at 135 °C. The polymer, confined and isolated in the trenches, has thus to nucleate homogeneously, this also influences the ferroelectric and piezoelectric properties of the P (VDF-TrFE) films.

4. Conclusion

In this work we have fabricated 1D line grating and 2D dot array nanostructures of ferroelectric P(VDF-TrFE) copolymer using nanoimprint lithography. The imprinted patterns also exhibit good ferroelectric and piezoelectric properties without annealing. Narrow domain lines were found near the trench edges due possibly to the high stress or drastic morphology variation. This technique has shown great potential in fabricating high density FeRAM or NEMS devices. Alternatively, the ferroelectric nanostructures could also be directly integrated in the gate stack of a field-effect transistor.

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