



Direct stamping and capillary flow patterning of solution processable piezoelectric polyvinylidene fluoride films



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ABSTRACT

It is well known that the potential applications of polyvinylidene fluoride (PVDF) mainly come from the piezoelectricity and ferroelectricity of its polar β phase. Thus, we have investigated the effect of different preparation conditions namely evaporation temperature, type of solvent and additive to enhance the β crystal structures of PVDF thin film. Subsequently, facile and direct soft lithography technique; direct stamping and capillary flow were employed to demonstrate good pattern transfer of PVDF thin films. The piezoelectricity of the microstructure was characterized using piezoresponse force microscopy (PFM) where fairly good piezoresponse was obtained without further processing procedures i.e., annealing or applied pressure/electric field. As such, our solution processable and direct patterning of PVDF techniques offer facile and promising route to produce arrays of isolated microstructures with improved piezoelectric functionality.

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1. Introduction

PVDF (polyvinylidene fluoride) is one of the semicrystalline polymers with its polymorphism characteristics of possessing four crystalline phases known for its pyroelectric, piezoelectric and ferroelectric properties [1–5]. PVDF exhibits different crystal phases largely depending on the processing and crystallization conditions. These different crystal structures include nonpolar orthorhombic α -phase, polar orthorhombic β -phase, monoclinic γ -phase, and δ -phase [6]. The most readily available α -phase, which has trans-gauche TGTG conformation is usually obtained from melt crystallization at atmospheric pressure whilst δ -phase can be obtained by polarizing α -phase with high electric field. On the other hand, γ -phase is usually obtained from high temperature crystallization with conformation intermediate of α - and β -phases [6]. Though α -phase being the most easily and commonly formed, the β -phase is the most highly sought among other crystals phase since it has all trans planar zigzag configuration (TTT) with enhanced pyro and piezoelectric properties. The β -phase is typically obtained by mechanical deformation of melt-crystallized films [6]. Other works which have successfully obtain β -phase PVDF include the molecular epitaxy on the surface of potassium bromide [7] crystallization at high pressures [8] and drawing of ultrathin PVDF films

prepared by melt blending [9]. However, these are not facile processes and some of which are arduous or not compatible to thin film processes. Furthermore, for the interest of large scale and practical thin film application, it is important to tune various polymorphs based on inexpensive and facile solution process with controlled and reproducible conditions.

Other than the processing conditions to tune the various polymorphs, patterned PVDF micro and nanostructures have attracted a great deal of interest for high density electronic, multiferroics, energy harvester, and microelectromechanical systems (MEMS) applications. Various techniques have been employed to pattern ferroelectric micro and nanostructures which include electron/ion-beam writing, self-assembling, nanoimprint and soft lithography [10–18]. While electron/ion-beam writing are able to pattern uniform arrays of nanostructures, the high processing cost, low throughput, and structural defects induced by the high energy ion/electron beam may alter/degrade the polarization in ferroelectric materials. On the other hand, though self-assembling of ferroelectrics molecules is an inexpensive process, precise control of patterned nanostructures over large-scale is often difficult to achieve. In recent years, soft lithography has emerged as promising techniques for fabricating functional nanostructures. Soft lithography involves pattern transfer with low cost, high throughput and fairly high resolution well-suited for large scale practical applications. The underlying pattern transfer mechanisms can either involve mechanical stamping of inking solution or chemical–

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physical processes between the elastomeric molds and capillary flow solution.

Here, we have investigated the effects of different preparation conditions namely evaporation temperature, type of solvent and additive on enhancement of β crystal structures of PVDF thin film. Subsequently, we employed facile direct stamping and capillary flow techniques to demonstrate the patterning of PVDF thin films. The piezoelectricity of the microstructure was characterized using PFM (Piezoresponse Force Microscope) where fairly good piezoresponse was obtained without further processing such as annealing or applied pressure/electric field, usually required for PVDF polymers processed from solution. Our method is beneficial since direct or one step printing or capillary flow produced isolated ferroelectric patterns without carrying out any harsh post processing which tend to degrade the functional properties of ferroelectrics.

2. Experimental details

2.1. Preparation of PVDF thin films

The organic solvents used were N, N-dimethylformamide (DMF) and mixed solvent of DMF and acetone (volume ratio 1:1). The PVDF powder (molecular weight $M_w \sim 534,000$) was dissolved in the organic solvents at 1–5 wt%. To completely dissolve the PVDF powder, the solution was heated at 50 °C in a water bath for 1 h. The precursor solution was kept at room temperature for sufficient time (12 h) to reach thermal equilibrium. The PVDF films were deposited by spin-coating the precursor onto silicon wafers at 1000 rpm for 30 s and dried at 25–100 °C for 1 h. As for the study on the effect of additive, 2 and 4 wt% of magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$ was added to the PVDF solutions followed by similar process as described earlier.

2.2. Preparation of pattern mold

Silicon wafer was cleaned in ethanol and isopropyl alcohol (IPA) ultrasonic baths sequentially to remove the organic contaminations. Positive photoresist S1805 was coated onto the substrate by spin-coating at 3000 rpm for 50 s followed by post-baking at 115 °C for 1 min. Exposure of the photoresist was conducted using a UV light source through a chrome mask for an exposure duration of 10–12 s. The developer used for the photoresist was MF319. The fabricated photoresist mold was used for stamping process.

In addition, the photoresist mold was used as template for Polydimethylsiloxane (PDMS) casting without additional pre-treatment. PDMS stamp was fabricated using Sylgard 184 silicone elastomer mixed with a curing agent (Dow Corning, USA) at a ratio of 10:1 by weight. The silicone elastomer mixture was then cast on a photoresist patterned Si master and evacuated in a vacuum jar. It was maintained at a pressure of 10^{-1} Torr for 20 min. This is to ensure that any trapped air bubbles were effectively removed. Finally, it was cured in a conventional oven at 60 °C for 24 h and the PDMS stamp was peeled off from the master. After the curing process, the PDMS mold was separated from the photoresist mold and used for capillary flow soft lithography patterning. All the patterning was carried out using PVDF of 2–3 wt % with DMF-acetone mixture.

2.3. Characterisation of PVDF

To determine the crystal structure of the as-prepared PVDF films, the X-ray diffraction patterns (XRD) were conducted (D8-ADVANCE, Bruker AXS GmbH, Karlsruhe). Fourier transform infrared (FTIR) spectra of the thin films were obtained from FTIR spectroscopy (Spectrum 2000, Perkin–Elmer) using reflectance

mode. Scanning electron microscopy (SEM) was used to observe the surface morphology of the PVDF films. The thicknesses of the films were determined from the SEM images of the cross section view. To study the piezoelectric effect of the as-prepared PVDF thin films or patterned PVDF, the samples were examined by PFM (MFP-3D, Asylum Research, Santa Barbara, CA, USA) for surface topographies and polarization characteristics under biased-voltage.

3. Results and discussions

The formation of PVDF crystalline structures and their surface morphologies depend on several factors which include organic solvent used, drying temperature of the spin-coated film and the addition of metal hydrates. The mixture of different α , γ and β crystals phase formation is dependent on the solvents used. DMF and acetone are used in this work since polar solvents usually give rise to thin films with dominantly β crystals [19]. It is important that PVDF of dominant ferroelectric β crystals is obtained in which parallel packing of all trans chains in an orthorhombic unit cell synchronizes chain rotation of the consecutive transconfiguration, i.e., TTTT sequence. β crystal provides the best polarization among other polymorphic crystalline structures of α and γ with the configurations of TGT-G and TTGT respectively [20]. The effect of solvent on the PVDF surface morphology was examined. Typical PVDF film surfaces resulting from the spin casting was observed to be rough and porous. From the SEM images of Fig. 1, it is evident that DMF-acetone solvent yields a less porous PVDF films than that when using the DMF solvent. It has been observed that DMF-acetone is good solvent of PVDF as such complete dissolution of PVDF with clearer solution can be obtained before spin coating. It is known that evaporation temperature is another important factor since it not only affects the structure of the films but also influences the piezoelectric functional properties [20]. Thus, other than the solvent, the effect of evaporation temperature (25 and 100 °C) on the PVDF thin film surface morphology was also studied. It is observed that in general low evaporation temperature results in grainy and porous films.

Fig. 2a presents the FTIR results for the PVDF thin films prepared under different conditions namely different solvents and evaporation temperatures. The dash lines on the graphs indicate the theoretical positions of the characteristic bands for each phase of PVDF. The characteristic absorption bands of α -phase PVDF are around 795 cm^{-1} , and bands of β -phase PVDF are around 840, 1275 cm^{-1} [20,21]. The γ -phase has an absorption band around 1233 cm^{-1} [22]. The relative amplitude of each peak indicates the amount of the phase presented in the PVDF thin film. From the transmission spectra, it can be seen that β phase is predominantly formed in the thin films that employed the use of DMF-acetone mixture solvent. PVDF film that are processed using high polar solvents will crystallize with the polar groups that tend to rotate the strong dipoles of the C–F bond in the PVDF molecular chain, and hence reduces the energy barrier for formation of expanded β all-trans conformation [19]. XRD spectra (Fig. 2b) were also obtained which show consistent result as the FTIR measurements where the use of DMF-acetone mixture solvent promotes β phase formation. It is observed that evaporation temperature also has an effect on the phase formation among the thin films prepared using the mixture of DMF-acetone solvent. The thin films dried at 25 °C shows enhanced β -phase compared to those dried at 100 °C. This is consistent with other report that the resulting crystalline phase depends on the crystallization rate, which in turn is determined by the evaporation rate of the solvent [20]. Low evaporation rates favor the formation of the trans-planar β phase. It is also noted that solvent evaporated at higher temperature of 100 °C exhibits enhanced α -phase peaks as such higher solvent evaporation temperature favors predominant trans-gauche α phase [20].

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