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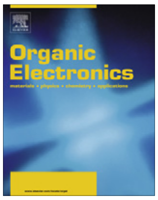

One-step micropatterning of highly-ordered semi-crystalline poly(vinylidene fluoride-*co*-trifluoroethylene) films by a selective shear and detachment process

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ABSTRACT

We present a one-step route for micropatterning a thin ferroelectric poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) film with both molecular and microstructural crystal control over a large area. The method is based on the static mechanical shearing and subsequent detachment of a film spin coated on pre-patterned Al which has been lithographically prepared on a SiO_2 substrate under appropriate thermal conditions. Selective detachment of the film in contact with the SiO_2 substrate gave rise to micropatterns of PVDF-TrFE film positioned only on the Al regions. Further, the PVDF-TrFE film showed 25-nm-thick crystalline lamellae aligned perpendicular to the shear direction, wherein the *c* axis of the crystals was globally ordered parallel to the shear direction. The sheared and patterned PVDF-TrFE thin films are readily incorporated into non-volatile memory units of metal/ferroelectric/metal capacitors and bottom gate-top contact field effect transistors, leading to arrays of memory devices with enhanced performance.

1. Introduction

Non-volatile memories fabricated from ferroelectric polymers such as poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) are of great interest among various organic non-volatile memory technologies such as flash [1,2] and resistive type ones [1,3] for potential use in organic information storage, one of the most essential technologies for realization of full organic electronic devices [4–6]. Solution-processed thin ferroelectric polymer films are easily incorporated into both destructive and non-destructive memory elements of metal/ferroelectric/metal (MFM) capacitors and ferroelectric field-effect transistors (FeFETs), respectively [4–12]. The macroscopic polarization of a ferroelectric film is attributed to the cooperative dipole moments pointing from fluorine to hydrogen in the ferroelectric polymer molecules, which are in turn hierarchically self-assembled into the characteristic crystalline structures. Non-volatile switching of the polarization is accomplished by rotating the polymer backbone around the chain axis upon exposure to a large polarization-opposing electric field [5].

There are, in our opinion, two main issues for realizing organic memories based on thin PVDF-TrFE films. First of all, in order to optimize ferroelectric properties such as remanent polarization, operating voltage, retention, fatigue and so on, the degree of crystallinity needs to be maximized. In addition, the effective crystal orientation in the *b* axis should be favorably aligned parallel to the electric field of the PVDF-TrFE [13–15]. Secondly, micropatterning of thin ferroelectric films should be possible

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such that microarrays of the memory elements are readily fabricated without harming the intrinsic properties of the PVDF-TrFE.

A globally oriented PVDF-TrFE thin film with effective crystal orientation has been achieved via various techniques which rely on the ability to couple an externally applied field to some molecular and/or supermolecular feature in the polymer. These techniques include crystallographic matching on a surface known as epitaxy [16,17], using a localized thermal gradient [18], directional solvent evaporation [19] and the employment of mechanical fields [20–22]. We have recently demonstrated two approaches for producing highly-ordered crystalline structures of ferroelectric polymer thin films spin coated onto substrates suitable for memory device architecture: high throughput epitaxy of a thin PVDF-TrFE film on a friction transferred poly(tetrafluoroethylene) (PTFE) surface [23] and global orientation of the film by static shear [24]. In particular, the static shear turned out to be very effective for centimeter scale orientation of the ferroelectric polymer without requiring an additional interlayer, which significantly increases the operating voltage.

Although photolithography with subsequent dry and wet etching processes, available in the current semiconductor industry, is the most common and is powerful for micropattern fabrication, it is, in general, not applicable to PVDF-TrFE patterning because the polymer is significantly damaged or suffers alteration of its intrinsic properties under the harsh patterning conditions. Great care should be taken when fabricating patterned structures of PVDF-TrFE using the conventional etching process [25]. Thus, there is a need for a new non-invasive method based on printing technologies. Several techniques have been demonstrated for micropatterning ferroelectric polymers, including microimprinting [26,27], capillary molding [28] and microcontact printing [19]. Ferroelectric blend layers have also been micropatterned by solid state transfer methods in which a thin blend film floated on a water/air interface was deposited onto metal-coated poly(dimethylsiloxane) pre-patterned mold, and, subsequently, both the ferroelectric and metal layers were directly transferred to another metal electrode surface, resulting in arrays of MFM capacitors [29]. A recent work by Sekitani et al. successfully demonstrated printed non-volatile ferroelectric memory for communication system based on solution processes including ink-jet printing [30].

Most of the previous works, including our approaches, are, however, limited to the fabrication of patterned ferroelectric polymers without successful control of crystal orientation in the patterned films. In other words, the micropatterns have semi-crystalline ferroelectric domains that are randomly oriented. It would be ideal to develop a non-invasive printing technique which is able to simultaneously control both the molecular structure and the microstructure of the ferroelectric crystals. Furthermore, the method would ideally have industrial potential when combined with the spin coating process, one of the most desirable methods for large area uniform polymer film formation.

In this study, we demonstrate a new one-step micropatterning technique which allows us not only to fabricate micropatterns of thin PVDF-TrFE films but also to control both the molecular and microstructural orientations of the ferroelectric crystals in the patterned regions. Our method is based on the static-shearing of a PVDF-TrFE film spin-coated onto a lithographically defined Al pre-pattern, followed by selective detachment of the film. Our shear and detachment process allows for the fabrication of a globally ordered crystalline structure of a PVDF-TrFE film on the pre-patterned Al regions in which the crystalline lamellae are globally oriented perpendicular to the shear direction. Furthermore, facile formation of thin patterned ferroelectric films on metallic surfaces with ordered crystalline structure enables us to fabricate arrays of both MFM capacitors and bottom-gate FeFET devices with enhanced memory performance.

2. Experimental section

2.1. Al patterned substrate preparation

Conventional photolithography was used to prepare various Al pre-patterns on SiO_2 substrates. First, a positive photoresist was spin-coated onto a 200-nm-thick SiO_2 grown wafer that had been chemically cleaned. After soft-baking to eliminate residual solvents, the photoresist was exposed to ultraviolet light through a photomask for development. Subsequently, an ~80-nm-thick layer of Al was deposited onto the patterned photoresist by thermal evaporation under a pressure of 10^{-6} mB at room temperature with a deposition rate of ~0.1 nm/s. The photoresist was then completely removed by lift-off. Finally, Al micropatterns with a variety of shapes and sizes were produced on the SiO_2 substrate, including 1.5-μm- and 5-μm-wide lines with periodicities of 5 and 10 μm, respectively, and 2 and 5 μm squares arrayed into a 4 mm symmetry. Hexagons with 2 μm sides were also prepared and arrayed into a 6 mm symmetry. For non-volatile memory devices, alternating Al lines 300 and 700 μm in width with a periodicity of 1500 μm were prepared on SiO_2 substrate through a shadow mask by thermal evaporation under the same conditions as described above.

2.2. Thin film preparation

The PVDF-TrFE with 27.5 wt% TrFE employed in our study was kindly supplied by MSI Sensor, PA. The melting (T_m) and Curie (T_c) temperatures of the polymer were 150 and 80 °C, respectively. PVDF-TrFE solutions in methylethylketone (MEK) with concentrations ranging from 1 to 5 wt% were spin-coated at a spin rate of 2000 rpm for 1 min to form thin polymer films on the micropatterned Al substrates.

2.3. Static shearing process

The same shearing process was applied for the current experiments as were used in our previous experiment [24]. A poly(methylsiloxane) (PDMS) pad 100 μm in thickness and $1.0 \times 1.0\ cm^2$ in size was placed onto the PVDF-TrFE film on a pre-patterned Al substrate. Then, the