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Letter

Topography engineering of ferroelectric crystalline copolymer film

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ABSTRACT

Effects of surface roughness as well as crystallinity onto functionalities of crystalline copolymer films were studied using a dipping method to inject the crystalline grains into voids among crystalline nano-rods. Differently from a widely-used fabrication method such as spin-coating of solution, we achieved a smooth surface and high crystallinity in ferroelectric P(VDF-TrFE) films, simultaneously. Varying dipping temperature and time, remnant polarization and relative dielectric constant values increased by 20% and 75% with a decrease of surface roughness from 20 nm to 7 nm in root mean square value, respectively. The ferroelectric stabilities of P(VDF-TrFE) film capacitors were found to be strongly dependent on the crystallinity.

1. Introduction

Crystalline organic films with features of convenience and low-cost manufacturing have alternated electronic devices which consist of crystalline inorganic materials with various functionalities arising from collective phenomena such as remnant polarization and dielectric constant [1–7]. However, the problem with organic device applications is that most crystalline organic films exhibit a rough topography consisting of nano-rods developed during crystallization [8–13], which results in degradation of electrical properties including poor remnant polarization and dielectric constant [12,14–16]. The rough topography of organic films is due, in microscopic aspect, to many voids with sizes of as large as hundreds of nanometers among the nano-rods. These voids interrupt the propagation of electrons and phonons such as electron transport and domain wall motion. In particular, for emergent organic electronics with embedded functional organic film, it is critical to develop a low-cost fabrication methodology that can fill the voids in organic films, which should lead not only to a smooth topography but also to enhanced functionalities of organic crystalline materials.

Crystalline poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] film with the largest remnant polarization (P_r) among organic ferroelectrics (FE) [17] is an ideal system to study whether its physical properties can be controlled by topographic properties including the size of voids as well as crystalline properties including phase density. The desirable electrical properties of P(VDF-TrFE) films which depend on these structural properties would be large values for P_r and dielectric constant (ε_r); however, few systematic studies have focused on the compromised effects of the topography and crystallinity of organic films. Basically, the topography of P(VDF-TrFE) film consists of either granules with a higher volume fraction of amorphous phase or nano-rods of crystalline FE beta (β) phase, depending on the annealing temperature (T) [8]. In nano-rod-based films, voids exist with a depth that approaches the total film thickness. In contrast, granular films contain no voids but low-angle grain boundaries, so that surface

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roughness, which is a measure of texture of surface, becomes smaller down to an order of a nanometer in root mean square (RMS) value. Both the FE P_r and ε_r of P(VDF-TrFE) film, even with a smaller volume fraction of FE crystalline β phase in granular topography, are not smaller than those in a nano-rod-based topography [12,18]. This indicates the importance of drastic change in topography with the formation of nano rods and voids on an entire surface during the crystallization process in determining the P_r and ε_r values of P(VDF-TrFE) films. Voids with a low ε_r induce a voltage drop [19,20] or promote leakage current as paths [12,21], resulting in a decrease in the overall P_r and ε_r of a P(VDF-TrFE) film.

In this work, we report a low-cost dipping process that can be used to fill the voids among the nano-rods of a P(VDF-TrFE) film capacitor device by injecting a low wt% of P(VDF-TrFE) solution. This process reduces the surface roughness of nano-rod-based films to a condition as smooth as that of granular films while conserving the crystalline FE β phase with nano-rods. We found that the dissolution of nano-rods during dipping can be minimized on a timescale that can amount to hours, which enabled us to sufficiently fill the voids. Granules with a few hundred nanometers in size adhere to the nano-rods during the dipping process, resulting in a smooth topography and a sharp interface in a metal/P(VDF-TrFE)/metal capacitor structure with an increase in the density of FE β phase of films by up to 46% by filling in the voids. We found that our fabrication technique combined the advantages of both granular and nano-rod-based P(VDF-TrFE) films, including large values for both P_r and ε_r, and enhanced endurance to fatigue and retention.

2. Experimental

2.1. Fabrication of copolymer films

We used a pellet-type P(VDF-TrFE) copolymer containing 50% TrFE (Piezotech, France). MEK (C_4H_8O, 99.5%, Sigma-aldrich) was used as a solvent for the copolymer because of its non-toxicity. The copolymer was dissolved at 80 °C for 1 h. The 5 wt% solution of P(VDF-TrFE) was spun on indium tin oxide (ITO)/ glass substrates for 30 s at a spin speed of 3500 rpm to fabricate a uniform film. Coated P(VDF-TrFE) films were annealed at 120 °C for 1 h in air using a furnace tube for the transformation to a high crystalline structure including nano-rods. The crystalline β phase was confirmed by X-ray diffraction using Cu Kα radiation from an Advanced D8 (Bruker, Germany).

2.2. Dipping process

We dipped high crystalline P(VDF-TrFE) copolymer films into a 2 wt% solution of P(VDF-TrFE) in order to achieve smooth the surface, and changed the dipping time and temperature. After dipping, every sample was spin-coated again for 30 s at 3500 rpm and post-annealed at 100 °C to crystallize the additionally injected solution on the films.

2.3. Morphological study

The surface topography of film was observed via AFM (Park XE-100, Park's System, Korea) in a non-contact mode. The RMS roughness was calculated using a PEI program provided from Park's System. Cross-sectional images were measured by dual beam-focused-ion beam/scanning electron microscopy (SEM) to compare the morphological results (Helios NanoLab 660, FEI, USA).

2.4. Grazing incidence X-ray diffraction (GIXRD)

GIXRD was performed on a 5D beam line at the Pohang Accelerator Laboratory in the using monochromatic X-rays (10 keV). Diffracted X-rays were detected using a pixel array detector (Pilatus 100 k, Dectris, Switzerland).

2.5. Electrical and piezoelectric characterization of film capacitor devices

To measure ferroelectric properties using a metal–ferroelectric material–metal (MFM) structure, 100 nm-thick Au top electrodes with 70 × 70 μm^2 in size were deposited through a shadow mask using an e-beam evaporator. Polarization (P)–electric field (E) hysteresis loops, fatigue, and retention of P(VDF-TrFE) films were measured using commercial ferroelectric measurement equipment (Precision LC, Radiant Technology). A 100 Hz triangular wave was applied to measure the P–E loops and fatigue. Retention tests were conducted using pulses that were 5 ms in width. Between writing and reading pulses, the films were baked at 60 °C on a hot plate. The piezoelectric properties were measured using a laser scanning vibrometer (OFV-3001-SF6, PolyTech GmbH).

3. Results and discussion

Fig. 1a–c shows the schematic diagrams of dipping process that was used to inject additional granular grains into the voids among crystalline nano-rods, leading to the combination of both structures. First, we prepared nano-rod-based films via the spin coating of P(VDF-TrFE) solution onto (ITO)/glass substrates with subsequent annealing at 120 °C (top panel of Fig. 1a). Second, we dipped films into the 2 wt% solution of P(VDF-TrFE) to fill the voids (Fig. 1b). Finally, we obtained a dipped film with additional granular grains after a crystallization process that was composed of additional spin-coating and subsequent post-annealing at 100 °C (see the Expermential Section 2).

We observed a change in the topography of P(VDF-TrFE) films during the dipping process using atomic force microscopy (AFM) images (Fig. 1d–f). Before the dipping, the nano-rod-based film consisted of nano-rods stacked together with diameters of approximately 200 nm. The size of voids was much larger than diameters of the nano-rods (Fig. 1d). The depth of the voids was less than 100 nm (Fig. 1g). The surface roughness was estimated to be 19.8 nm in root mean square (RMS) value over an area of 5 × 5 μm^2. After dipping in a 2 wt% solution of P(VDF-TrFE) at 25 °C for 1 h and a crystallization process, we observed