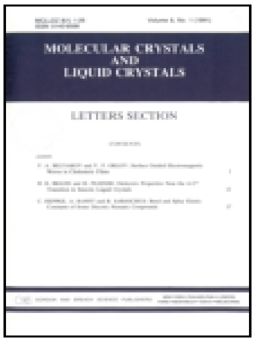

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Asymmetric Ferroelectric Switching Based on an Al/PVDF Langmuir-Blodgett Nanofilm/PEDOT:PSS/Al Device

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We prepared highly oriented ferroelectric poly(vinylidene fluoride) (PVDF) Langmuir–Blodgett (LB) nanofilms by an assistance of amphiphilic poly(N-dodecylacrylamide) (pDDA) nanosheets. In the nanofilms, semi-crystalline PVDF contains abundant polar β crystals, a parallel packing of PVDF all-trans molecules. Combing semi-conductive PEDOT:PSS and ferroelectric PVDF LB nanofilms, we fabricated a sandwiched capacitor (Al/PVDF LB nanofilm/PEDOT:PSS/Al). The capacitor shows asymmetric hysteresis curves and high remanent polarization values.

Keywords Ferroelectricity; poly(vinylidene fluoride); Langmuir-Blodgett film

Introduction

Because of good ferroelectricity, poly(vinylidene fluoride) (PVDF) based polymers appeal to active researches for nonvolatile memories. PVDF is a semi-crystalline polymer, consisting of different crystal structures, for instance, α, β, γ, δ, and ε phases [1]. Of all the phases, β crystals, an arrangement of molecules with all-trans conformations (Fig. 1) devote to piezoelectricity, pyroelectricity, and ferroelectricity of PVDF-based materials [2,3]. The β crystal takes an orthorhombic unit cell with the lattice parameters of $a = 8.47$ Å, $b = 4.90$ Å, and c (chain axis) $= 2.56$ Å [4]. Aiming at high data density, low-voltage and flexible devices, studies on PVDF nanofilms become more and more important. However, difficulties in thin film preparation, reduced crystallinity of PVDF in the nanofilms and large porosity are the main constraint for its further applications. In our previous report, we introduced a facile method to prepare highly oriented PVDF LB nanofilms assisted by amphiphilic polymer nanosheets [2]. Those nanofilms show adjustable film thickness by 2.3 nm, high film density storage and good electric response ability. Furthermore, the as-deposited PVDF LB nanofilms show remarkably high remanent polarization (P_r), about

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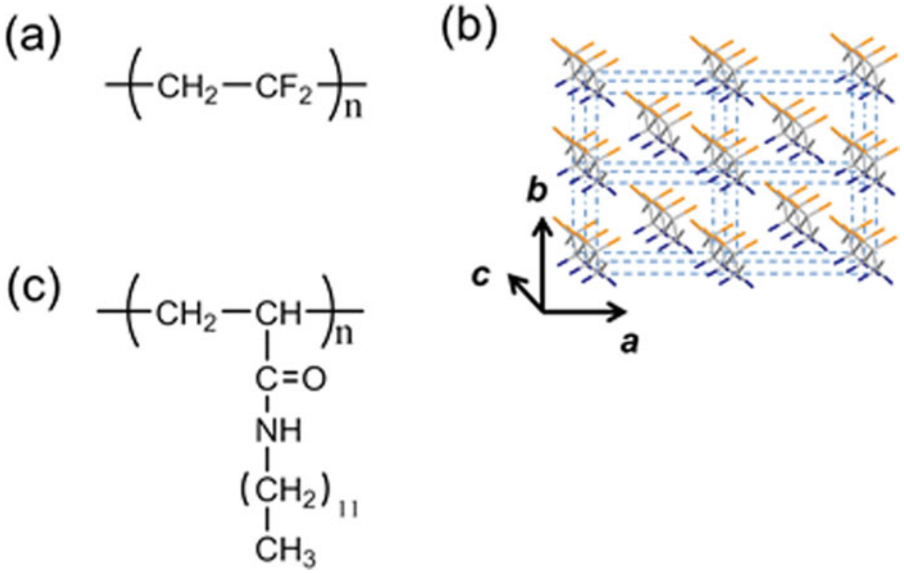

Figure 1. (a) Chemical structure of PVDF, (b) crystal structure of β-phase PVDF (F, orange; C, gray; H, blue), and (c) chemical structure of pDDA.

6.6 μC cm^{-2} at 81 nm and extrinsic switching characteristics [5]. Based on the PVDF LB nanofilms, the present study demonstrates asymmetric ferroelectricity of nanocapacitors with a structure of Al/PVDF LB nanofilm/PEDOT:PSS/Al. They show asymmetric remanent polarization (P_r) values, which are a $+P_r$ value of 6.0 μC cm^{-2} and a $-P_r$ value of -15 μC cm^{-2}. The -P_r value is the largest remanent polarization value ever reported for PVDF homopolymer nanofilms.

Experimental Section

PVDF ($M_n = 7.1 \times 10^4$, PDI = 2.5) (Aldrich) was used after a reprecipitation from DMF (Wako Pure Chemical Industries Ltd.) to methanol (Wako Pure Chemical Industries Ltd.). pDDA ($M_n = 3.0 \times 10^4$, PDI = 3.0) was synthesized through free radical polymerization initiated by 2, 2′-azobisisobutyronitrile (AIBN). Surface pressure (π)–area (A) isotherms of pure pDDA, pure PVDF and PVDF:pDDA (50:1, molar ratio) Langmuir films were recorded at a compression rate of 14 cm^2/min at 20°C using an automatically controlled Langmuir trough (FSD-220&21; USI Corp.). An aluminium (Al) wire for electrode evaporation was purchased from the Nilaco Corporation, Japan with a diameter of 0.30 mm. Ferroelectric nanocapacitors (FeNCs) with a device structure of Al/PVDF LB nanofilm/PEDOT:PSS/Al were constructed, in which the PVDF LB nanofilm was 81-nm thick. Top and bottom Al electrodes (55 ± 5 nm) with area of 3 mm × 3 mm were thermally evaporated through a metal mask at a rate of 1.0 Å s^{-1} (TSU062H, Balzers, Germany). The sample was cooled using liquid nitrogen at 77 K during the deposition of the Al top electrode. The PEDOT:PSS aqueous solution (Aldrich) was spin-coated at 2500 rpm for 30 s onto the LB nanofilm to form an insertion layer. Displacement (D)–electric field (E) hysteresis loops

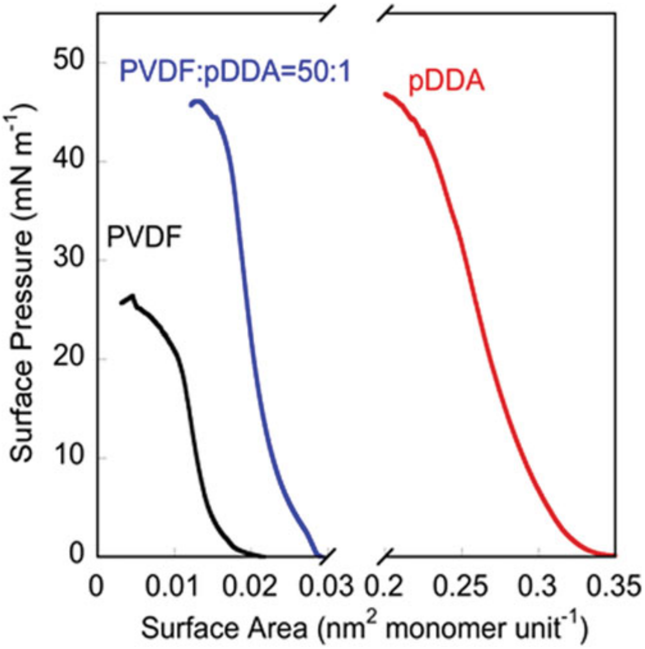

Figure 2. Surface pressure (π)–area (A) isotherms of pure pDDA (red line), pure PVDF (black line) and PVDF:pDDA at a molar ratio of 50:1 (blue line).

were characterized using a traditional Sawyer–Tower method with a triangle waveform voltage at a frequency of 1 Hz with a reference capacitor of 1 μF [6,7].

Results and Discussion

Figure 2 shows the π–A isotherms of pDDA, PVDF and PVDF:pDDA at a molar ratio of 50:1. After introducing pDDA into PVDF Langmuir film, the π–A isotherm of PVDF:pDDA Langmuir film presents a steep rise and a highly enhanced collapse surface pressure up to 45 mN m^{-1}, which indicates the stable film properties at the air–water interface [2,8,9]. The PVDF:pDDA Langmuir film was transferred onto the substrates using vertical dipping at a dipping speed of 10 mm/min. The deposition pressure was 30 mN/m. The monolayer thickness was reported as 2.3 nm. The PVDF:pDDA LB nanofilms were characterized with a high crystallinity of 52% and a high content of β crystal up to 95% [2]. Because of the tiny content of pDDA, we use the term of PVDF LB nanofilm to replace PVDF:pDDA LB nanofilm for short. The AFM image of the 81-nm thick PVDF LB nanofilm on the Al bottom electrode show a root mean square (RMS) roughness of 10.91 nm and fiber structures (Fig. 3a). After spin-coating PEDOT:PSS, the film roughness was increased to be 13.42 nm (Fig. 3b).

The ferroelectric device has a structure as shown in Fig. 4a, in which a PEDOT:PSS layer is inserted between the 81-nm thick PVDF LB nanofilm and the Al top electrode. The PEDOT:PSS layer is a hole-only (electron blocking) transport layer, which has a chemical structure shown in Fig. 4b. Ferroelectricity was characterized with a triangle waveform voltage at different voltage amplitudes (Fig. 4c), which shows asymmetric displacement (D)–electric field (E) hysteresis loops with a gradually saturated shape. The dependence of

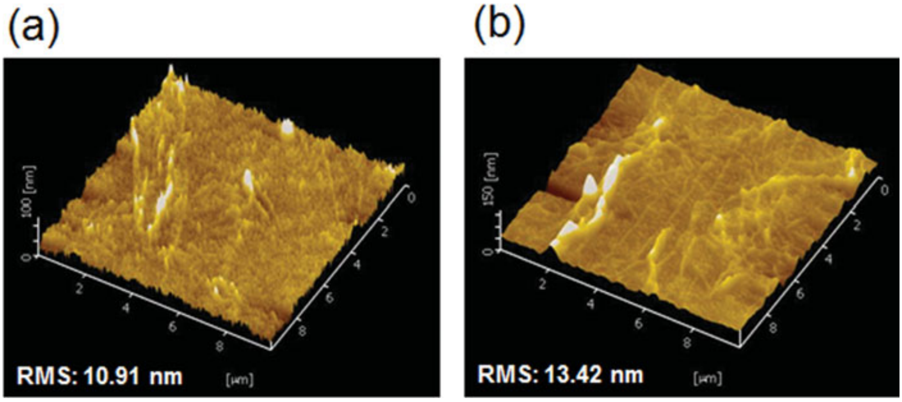

Figure 3. Surface morphologies of (a) 81-nm LB nanofilm and (b) spin-coated PEDOT:PSS on the LB nanofilm.

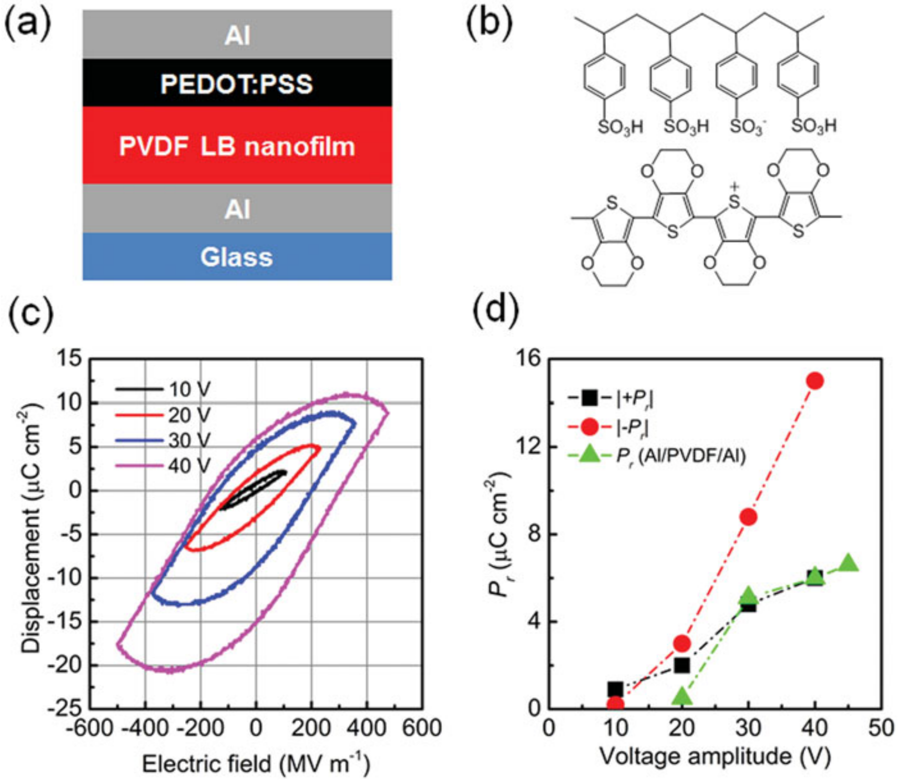

Figure 4. (a) Layer structure of the PEDOT:PSS inserted FeNC, (b) chemical structure of PEDOT:PSS, (c) hysteresis loops of the FeNC at 1 Hz with different applied voltage amplitudes, and (d) P_r values at different applied voltage amplitudes. The line serves as a visual guide.

absolute P_r values on the electric field was plotted in Fig. 4d. The values show an increasing tendency with the increasing of electric field, which is in good agreement with reference reports [10]. The reason is that the dipole moments of PVDF are slightly oriented in the films at a low electric field. When a high electric field is applied, the dipole moments are highly oriented, thereby leading to a large remanent polarization.

From the hysteresis loops, the remanent polarization (P_r) values are asymmetric with alternating electric field for the capacitor with the PEDOT:PSS layer, for instance, a positive remanent polarization ($+P_r$) value of 6.0 μC cm^{-2} and a negative remanent polarization ($-P_r$) value of -15 μC cm^{-2} at an applied voltage amplitude of 40 *V* (Fig. 4d). This result is different from that of a device of Al/PVDF LB nanofilms/Al, which shows symmetric hysteresis loops as previously reported [5]. The absolute value of -P_r, $|$-$P_r|$ is even larger than the theoretical value ever reported for β-phase PVDF, about 13 μC cm^{-2} [3]. Asadi *et al*, reported a diode with a Ag/PVDF:P3HT/LiF/Au capacitor, which shows asymmetric hole accumulation properties from the metal electrode to PVDF:P3HT by modulating ferroelectric polarization direction under positive or negative polarization [11]. The asymmetric *D-E* curves of the device in the present study might be also related to the unfavorable and favorable charge accumulation in the PVDF/PEDOT:PSS interface, modulated by the polarization direction of PVDF LB nanofilms. When the top electrode is negatively biased, hole accumulation is unfavorable at the interface, because of the increased injection barrier and electrostatic repulsion by the polarized PVDF dipoles,[11] thereby resulting in $|+P_r|$ values close to the values of a device with a structure of Al/PVDF LB nanofilm/Al (Fig. 3d(triangle data)). In contrast, when the top electrode is positively biased, hole accumulation is favorable at the interface due to the opposite polarization direction of the aligned PVDF dipoles. Finally, the total polarization value (D_{total}) is attributed to two components of the accumulated charge (D_{semi}) in PVDF/PEDOT:PSS interface and the dipole polarization (P_{PVDF}) of ferroelectric PVDF, thereby leading to higher $-P_r$ values (Fig. 3d).

Conclusion

A PVDF ferroelectric nanocapacitor was prepared with a device structure of Al/PVDF LB nanofilm/PEDOT:PSS/Al, which shows asymmetric hysteresis loops. This asymmetric property may originate from the charge accumulation in the PVDF/PEDOT:PSS interface layer. It led to different remanent polarization values of 6.0 μC cm^{-2} for $+P_r$ and -15 μC cm^{-2} for $-P_r$. This peculiar discovery sheds light on the diode applications of ferroelectric materials.

Acknowledgments

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