

Fabrication and Properties of Solution Processed All Polymer Thin-Film Ferroelectric Device

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ABSTRACT: A ferroelectric device, making use of a flexible plastic, polyethyleneterephthalate (PET), as a substrate was fabricated by all solution processes. PET was globally coated by a conducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) acid (PEDOT/PSSH), which is used as bottom electrode. The ferroelectric copolymer, poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), thin film was deposited by spin-coating process from solution. The top electrode, polyaniline, was coated by solution process as well. The ferroelectric properties were measured on this all solution processed all polymer ferroelectric thin-film devices. A square and symmetric hysteresis loop was observed with high-polarization level at 15-V drive voltage on a all polymer

device with 700 Å (PVDF-TrFE) film. The relatively inexpensive conducting polyaniline electrode is functional well and therefore is a good candidate as electrode material for ferroelectric polymer thin-film device. The remnant polarization P_r was 8.5 $\mu\text{C}/\text{cm}^2$ before the fatigue. The ferroelectric degradation starts after 1×10^3 times of switching and decreases to 4.9 $\mu\text{C}/\text{cm}^2$ after 1×10^5 times of switching. The pulse polarization test shows switching take places as fast as a few micro seconds to reach 90% of the saturated polarization. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1510–1513, 2011

Key words: fluoropolymers; ferroelectricity; conducting polymer; printed electronics; random access memory

INTRODUCTION

Ferroelectric devices based on polymer thin films have attracted a great deal of attention recently due to their applications in electronics, photonic, micro-sensors, and actuators.^{1–5} Ferroelectric polymer random access memory (RAM) in low cost is one of the most proposed applications due to the ease of processing through spin casting or printing at low temperature combining with low-voltage operation by the use of ferroelectric polymer in thin-film forms.

The ferroelectric properties are directly related to the crystallinity and crystallite size in the ferroelectric polymer film. It is expected that the surface and interface will play a significant role in the development of morphology and chain conformation of the films as the polymer film thickness reduced.^{6,7} It is believed that, in thin films, the crystallization will be hindered due to the heterogeneous nucleation process from the stiff metal substrates. If the electrode

is conductive polymer, due to their softness, the restrictions of crystallization of ferroelectric polymer may reduce. We reported an all polymer ferroelectric devices with free standing thick poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) film and conducting polymer, which works well.⁸

On the other hand, printed electronics is an emerging industry.^{9–14} Contrary to the processes that are used to manufacture traditional electronics, such as photolithography and chemical etching, printed electronics uses a printing process to deposit “functional inks” resulting in a much more efficient way, because materials are deposited only where necessary. The fully printed electronics concept opens up whole new markets for low-cost, disposable products with a functionality that was previously thought impossible.

One such application area is memories for RFID tags where price is of utmost importance.

In this work, we report a ferroelectric device, which can be used as a single-cell memory device, fabricated by all solution process with all polymer materials. A flexible plastic, polyethyleneterephthalate (PET), which uses as a substrate, was globally coated by a conducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) acid (PEDOT/PSSH), which is used as bottom electrode. The ferroelectric copolymer PVDF-TrFE thin film with molar ratio of VDF/TrFE 70/30 was deposited by spin-

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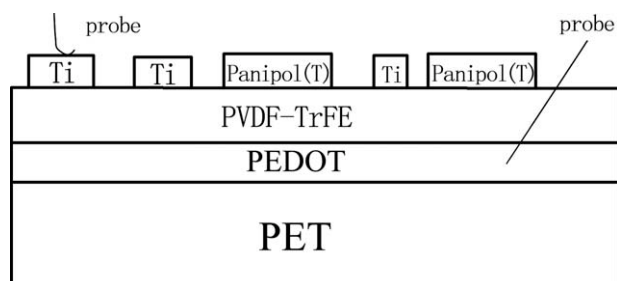


Figure 1 The cross section view of the ferroelectric thin-film devices.

coating process from solution. Polyaniline, a conducting polymer, which uses as the top electrode, was coated by solution process as well.

EXPERIMENTAL

Sample preparation

A flexible PET substrate with a bottom electrode of a conducting polymer, PEDOT, was purchased from Agfa Gevaert (trade name Orgacon). The PET substrate was cleaned by acetone and deionized water to remove contaminations and particles and then dried by a flow of nitrogen. The ultrathin films of PVDF-TrFE copolymer, with a molar ratio 70 : 30 for the VDF:TrFE monomers, were deposited by spin-coating technique from a 2.5% diethyl carbonate solution at 3000 rpm. The solvent was heated up if necessary to dissolve PVDF-TrFE powder. The solution is stirred until all polymer powder is dissolved and was filtered in advance using 0.1- μm filters. The resulting polymer film was annealed in a convection oven for 30 min at the temperature of 130°C. To determine the thickness of PVDF-TrFE thin films, a reference sample on silicon wafer was spin coated with identical PVDF-TrFE solution at the same conditions. A top electrode is then applied by the deposition of a droplet of a conducting polymer liquid, polyaniline toluene solution from Panipol Finland. The sample was heated on a hot plate at 80°C for 5 min to evaporate solvent. For comparison of ferroelectric properties, a top metal electrode, titanium, was deposited by vacuum evaporation on the identical sample. Ti was evaporated through a shadow mask having circular openings with diameter of 280 μm . The thickness deposited of Ti was 900 Å. To measure the conduction behavior of commercial polyaniline from Panipol, polyaniline film with 1000 Å thickness was spin coated on clean PET substrate, and top electrodes were deposited by vacuum evaporation. Two types of electrode material, Ti and Au, were tested.

Measurement

The thickness of PVDF-TrFE thin film, 700 Å, was determined by α -step 500 surface profiler (Tencor

Instruments). The temperature dependence of resistance of polyaniline was tested, because many devices work at temperature higher than room temperature due to the heat effect. The polarization hysteresis loops were recorded on Precision Pro Ferroelectric tester manufactured by Radiant Technologies, using Sawyer-Tower technique with an external electric field in the form of triangular wave with a frequency of 10 Hz. The drive voltage in these measurements is 15 V. Pulse polarization and fatigue data are recorded at room temperature. Pulse length is 50 μs for pulse polarization measurements and fatigue testing. The drive voltage is 15 V, and the fatigue was measured with 1×10^5 switching cycles. Figure 1 shows the cross section view of the ferroelectric thin-film device. The probe on top electrode is a soft silver wire while the probe on bottom electrode is sharp.

RESULTS AND DISCUSSION

Conductive properties of polyaniline

Polyaniline is one of the most promising conducting polymers for industrial applications, because it is relatively inexpensive and has high stability in air as well as relatively high conductivity. Moreover, commercially available polyaniline solution or suspension is printable. Different printing methods, for example, screen printing, flexo, gravure, lead to mass production and low cost. The resistance at different temperature of a 1000-Å thick polyaniline thin film on PET was shown in Figure 2. The commercial Panipol polyaniline shows unusual metal-like behavior, and the resistance increases with the temperature. Normally polyaniline has semiconductor-like temperature dependence. Polyaniline electrode is functional as the working temperature is below 90°C. The results showed that polyaniline is a good

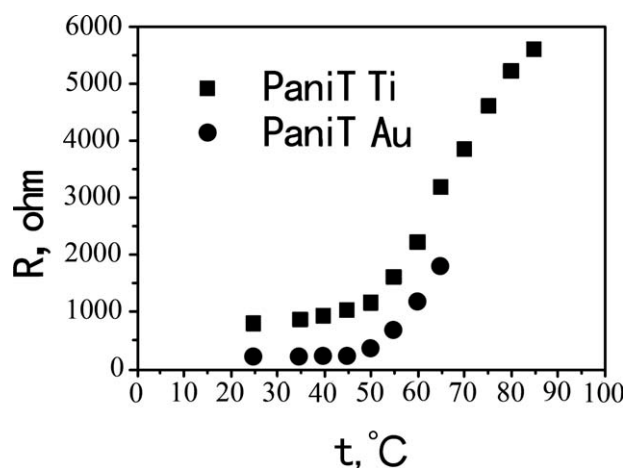


Figure 2 Temperature dependence of resistance of PaniT on PET with top Ti and top Au.

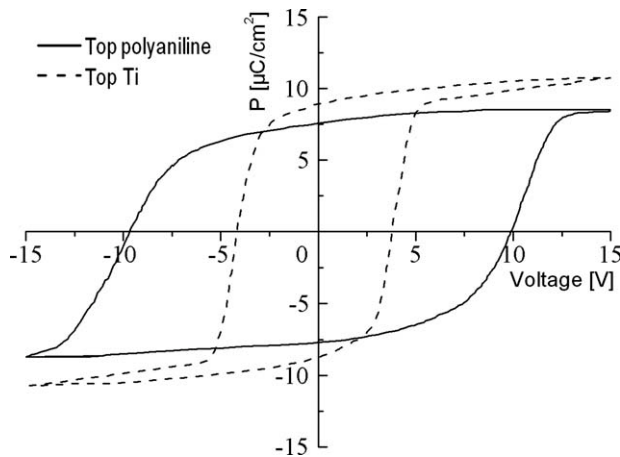


Figure 3 The hysteresis loop of PVDF-TrFE thin-film devices.

candidate as electrode material for ferroelectric polymer device, because the current is low when the device works.

The polarization hysteresis loops

Figure 3 shows the hysteresis loops for ferroelectric devices with polyaniline and Ti top electrode, which are the typical hysteresis loops of PVDF-TrFE copolymer ferroelectric films. For all polymer ferroelectric devices, the coercive voltage 9.19 V before fatigue was recorded. There is 0.17 V of asymmetry of the coercive voltage, which means that the polarization loop was symmetry, because both bottom and top electrodes are conducting polymer. The driving voltage is 15 V, which meets the requirement of many applications; for example, single-cell memory, chipless radio frequency tag, game card, and toy. However, comparing with devices with top Ti electrode, the coercive voltage of polyaniline devices (9.19 V) is much higher than that of Ti device (3.88 V), and the remnant polarization of polyaniline devices is lower than that of Ti devices. On the other hand, Ti devices show higher remnant polarization ($8.9 \mu\text{C}/\text{cm}^2$) than that of polyaniline device ($7.6 \mu\text{C}/\text{cm}^2$). For the practical applications, lower coercive voltage (therefore, lower driving voltage of the devices) and higher polarization are desired. The increase of conductivity of conducting polymer will improve the performance of the ferroelectric device. Attention should be paid to the contact between the probe and top electrode during the electrical measurement. Water-based polyaniline, Panipol W, electrodes show very good contact with probe wire. However, worse wettability of water-based conducting polymer with ferroelectric film was observed. On the other hand, organic solvent (e.g., toluene and xylene) based conducting polymers show better wettability and adhesion with PVDF-TrFE film but worse contact with probe.

The fatigue properties

Fatigue property is one of the important parameters related to the performance of ferroelectric devices. Figure 4 shows the fatigue of the thin-film ferroelectric devices at room temperature. For the devices with Ti as top electrode, the polarization P was $8.5 \mu\text{C}/\text{cm}^2$ and remained unchanged before 1×10^4 times of switching. The ferroelectric degradation starts thereafter and decreases to $7.5 \mu\text{C}/\text{cm}^2$ after 1×10^5 times of switching. The ratio of P before and after fatigue test was 0.88. Figure 4 also shows the fatigue of the sample with top polyaniline electrode at room temperature, and the polarization P was $7.4 \mu\text{C}/\text{cm}^2$ before the fatigue and remained unchanged before 1×10^3 times of switching. The ferroelectric degradation starts thereafter and decreases to $4.9 \mu\text{C}/\text{cm}^2$ after 1×10^5 times of switching. The ratio of P before and after fatigue test was 0.58. Although for many low end applications, 1000 times of switching (reading and writing cycles) are more than enough, high conductivity of top electrode are desired for high-end applications of ferroelectric devices.

In ferroelectric polymer, fatigue usually include "inherent" fatigue, which is determined by the polymer itself; "external" fatigue, which is determined by the interlayers, used between ferroelectric polymer and electrodes; "interface" fatigue, which is determined by the changes due to incompatibility of the electrode-polymer junction, for example, chemistry at this interface, degradation of the polymer surface caused by strong electric fields surrounding cracks in top electrode, and delaminating. To improve the fatigue properties, it is needed to test different choice of polymer and electrode material. Interlayer between electrode and ferroelectric thin film is also critical to improve fatigue properties. We reported that an interface layer between electrode and ferroelectric polymer improve fatigue properties, the remnant polarization is stable even after more than 100 million times of switching.¹⁵

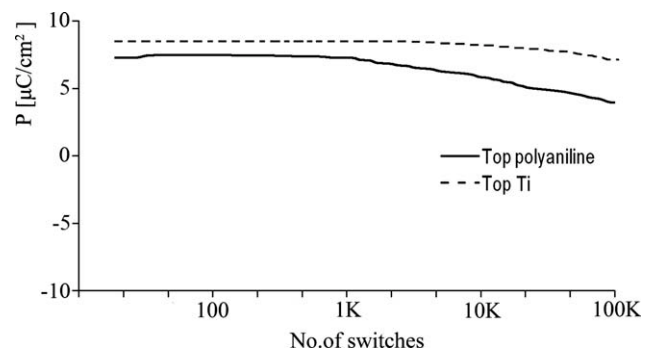


Figure 4 The fatigue cure of PVDF-TrFE thin-film devices.

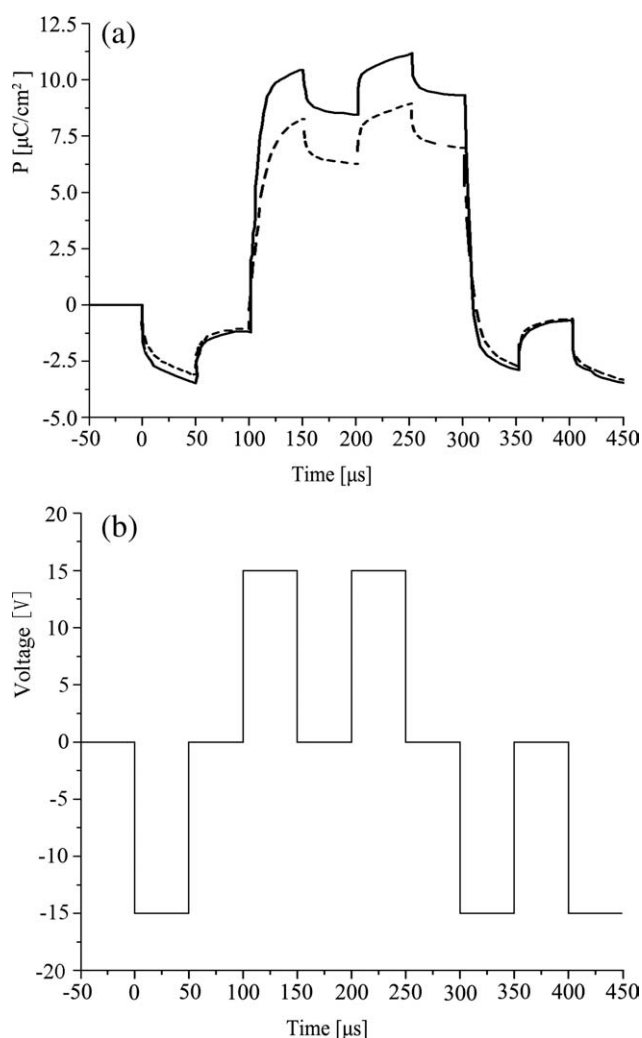


Figure 5 (a) The pulse polarization of PVDF–TrFE thin-film devices with top conducting polyaniline electrode. (b) Pulse sequence used to probe ferroelectric materials consisting of a negative preset pulse followed by two positive pulses and two negative pulses.

Pulse polarization

It is of great interest how fast the polarization can be switched when ferroelectric capacitors are applied in nonvolatile ferroelectric RAMs, because the memory is based on their switchable remnant polarization, which can be reversed by application of a short voltage pulse.¹⁶ Figure 5(a) shows the pulse polarization measured on the all polymer ferroelectric PVDF–TrFE thin-film devices with top polyaniline electrode. The shape of pulse train, so-called positive up negative down (PUND) measurement, was shown in Figure 5(b). PUND is a standard pulse sequence used to probe ferroelectric materials consisting of a negative preset pulse followed by two positive pulses and two negative pulses.

The solid line is the pulse polarization curve before the fatigue, and the dashed line shows the polarization curve measured after 1×10^5 times of switching. Comparing with a polarization switching time of as

fast as 220 ps,¹⁷ the polarization switching is much slower in thin ferroelectric PVDF–TrFE film with conducting polymer as electrodes. At pulse with 50 μs, there is still no total switching. After 1×10^5 times of switching, the switching speed is slowed down. Although the switching speed meets the requirement for the all polymer thin-film ferroelectric devices, which are used in low-end memory, it is highly desired to improve the switching speed for high-end nonvolatile ferroelectric RAMs application.

CONCLUSIONS

An all-polymer ferroelectric thin-film device was fabricated on a flexible PET substrate by all solution processes, which may lead to the mass production process by printing. The ferroelectric measurement shows a square and symmetric hysteresis loop with high-polarization level at 15-V drive voltage. The pulse polarization test shows that the switching speed in thin ferroelectric polymer film is much slower than that in thin-film inorganic ferroelectrics. The results imply that relatively inexpensive conducting polyaniline electrode is functional and therefore is a good candidate as electrode material for ferroelectric polymer device. Higher conductivity of top electrode and faster switching speed are desired for high end applications of ferroelectric devices.

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