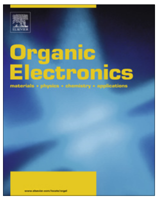
Organic Electronics 15 (2014) 22–28

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Characterization of current transport in ferroelectric polymer devices

Amir N. Hanna [1], Unnat S. Bhansali [1], M.A. Khan, H.N. Alshareef *

Materials Science & Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

ARTICLE INFO

Article history:
Received 19 June 2013
Received in revised form 7 October 2013
Accepted 9 October 2013
Available online 4 November 2013

Keywords:
P(VDF-TrFE) capacitors
Charge injection
Charge-transport mechanisms
I–V analysis

ABSTRACT

We report the charge injection characteristics in poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE), as a function of electrode material in metal/ferroelectric/metal device structures. Symmetric and asymmetric devices with Al, Ag, Au and Pt electrodes were fabricated to determine the dominant carrier type, injection current density, and to propose transport mechanisms in the ferroelectric polymer. Higher work function metals such as Pt are found to inject less charges compared to lower work function metals, implying n-type conduction behavior for P(VDF-TrFE) with electrons as the dominant injected carrier. Two distinct charge transport regimes were identified in the P(VDF-TrFE) devices; a Schottky-limited conduction regime for low to intermediate fields ($E < 20$ MV/m), and a space-charge limited conduction (SCLC) regime for high fields ($20 < E < 120$ MV/m). Implication of these results for degradation in P(VDF-TrFE) memory performance are discussed.

1. Introduction

P(VDF-TrFE) is a promising material for flexible organic non-volatile memory applications [1]. Nonvolatile ferroelectric random access memories' (FRAM) operation is based on the polarization reversal of electric dipoles in this polymer by an external applied electric field. The computational "0" and "1" are represented by the nonvolatile storage of negative or positive remnant polarization state, respectively, in the polymer material. Reading of the memory state is done by measuring the current through the ferroelectric material, which exhibits either a high conductance state or a low conductance state [2]. Despite easy operation and fabrication, the two major problems facing this type of memory are (a) polarization fatigue, defined as the reduction or the loss of remnant polarization under electric field cycling and (b) data retention. Both of these phenomena determine the long-term reliability of memory devices and are known to be affected mainly by two factors: (i) the depolarization field inside the film and (ii) the charge injection into the film [3]. Hence, it becomes critically important to identify and thoroughly understand the charge injection and transport mechanisms in these polymer ferroelectric thin films.

For inorganic ferroelectrics such as $Pb(Zr_x, Ti_{1-x})O_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT), polarization fatigue is a well-studied phenomenon believed to depend strongly on charge injection into the ferroelectric film [4,5]. However, in the case of organic ferroelectrics such as P(VDF-TrFE), charge transport and the role of charge injection in device performance has not been thoroughly characterized. Bihler et al. reported that charge injection and trapping at polarized crystallite surfaces is essential to stabilize the remnant polarization [6], but no comments were made on the fatigue performance due to charge injection. Xia and Zhang reported that charge injection in P(VDF-TrFE) is interface-controlled and a Schottky barrier forms at the metal-polymer interface [7]. He also reported that higher work function metals have lower injection barrier compared to lower work function metals, suggesting a p-type behavior for charge transport. Other reports in the literature have also suggested Schottky emission as the limiting

---

* Corresponding author.
E-mail address: husam.alshareef@kaust.edu.sa (H.N. Alshareef).
[1] These authors contributed equally to this work.

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.10.009

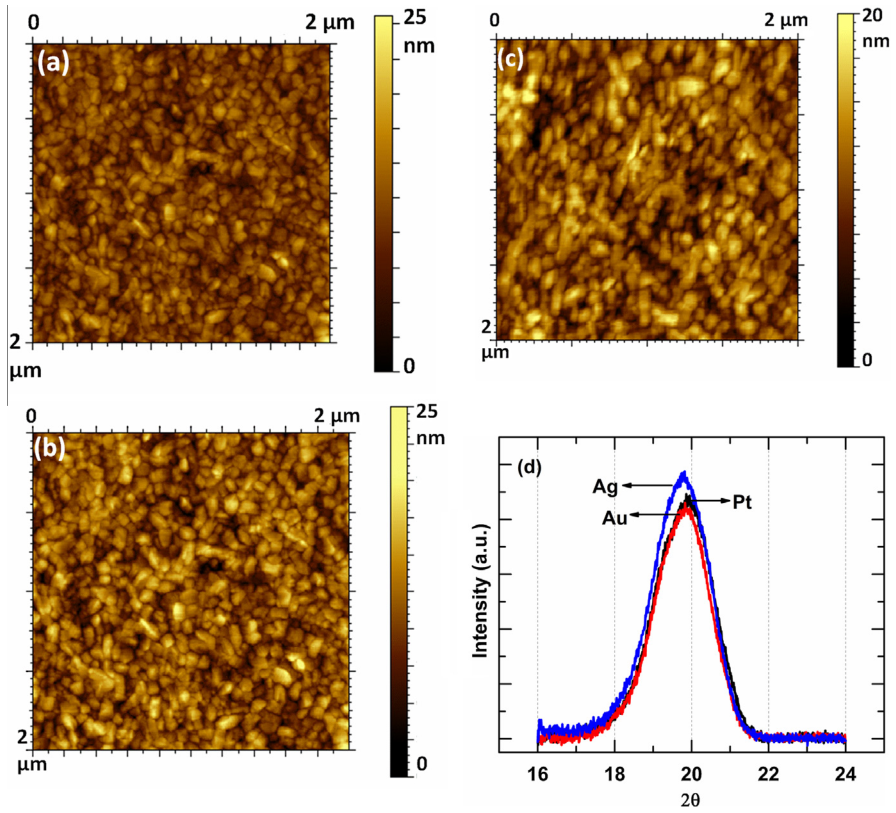


Fig. 1. Hysteresis curves measured at 10 Hz for (a) symmetric devices with Au and Ag as electrodes and (b) asymmetric devices with Pt as the bottom electrode and Au, Ag and Al as the top electrode.

leakage mechanism in P(VDF-TrFE) capacitors [8]. However, our data suggests n-type transport behavior in P(VDF-TrFE) thin films contrary to what has been reported earlier by Xia and Zhang [7]. Clearly, there seems to be a lack of complete characterization of the leakage behavior, charge injection and transport mechanisms in P(VDF-TrFE), specifically as a function of electrodes and temperature. Therefore, we have conducted a detailed study to characterize the leakage current behavior of P(VDF-TrFE) films sandwiched between electrodes of similar or dissimilar work functions, and propose charge transport mechanisms in P(VDF-TrFE) over a range of conditions.

2. Experimental

Prior to fabrication, Si substrates coated with 100 nm SiO_2 were cleaned by ultrasonication in acetone, isopropanol and de-ionized (DI) water for 10 min each. The substrates were then cleaned in Oxygen plasma for 5 min. prior to depositing the bottom electrode. Bottom Au and Ag electrodes, ~100 nm thick were deposited by thermal evaporation. The P(VDF-TrFE) (70–30 mol.%) was dissolved in anhydrous methyl ethyl ketone (MEK) at a concentration of 30 mg/mL to get a 3 wt.% solution. Thin films of P(VDF-TrFE) were spin-coated on all substrates at 6000 rpm for 60 s and baked on a hotplate at 80 °C for 30 min followed by annealing in vacuum at 140 °C for 4 h. The samples were allowed to cool down in vacuum to room temperature to facilitate the ferroelectric β phase growth. The thickness of the films was measured to be 220 + 10 nm, using a Dektak profilometer. Top Au, Ag and Al electrodes were deposited by thermal evaporation through a shadow mask. The electrical characterization was done using the Keithley 4200 Semiconductor Parameter Analyzer. The temperature-dependent current–voltage (*I*–*V*) characteristics of the devices were measured by heating the sample holder from 25 to 65 °C. All the *I*–*V* data shown represent averages of five devices of similar area. The *I*–*V* curves are reported after two initial sweeps, to make sure that steady state *I*–*V* curves are obtained.

3. Results and discussion

Fig. 1(a)–(c) shows the AFM topography images of our spin coated P(VDF-TrFE) films on Pt, Au and Ag (c) substrates, respectively. The surface morphology show extremely smooth and homogeneous films with an average R_{rms} roughness of ~2.9 nm, 2.8 nm and 2.6 nm on Pt, Au and Ag substrates, respectively. We also characterized the films using scanning electron microscopy (see Supplementary information). The films spun on different electrodes showed similar nucleation and grain growth behavior. The average grain size was similar and as determined from the SEM images was ~115 ± 10 nm on Pt, 120 ± 10 nm on