

Temperature dependence of electronic transport property in ferroelectric polymer films

X.L. Zhao, J.L. Wang*, B.B. Tian, B.L. Liu, Y.H. Zou, X.D. Wang, S. Sun, J.L. Sun*, X.J. Meng, J.H. Chu

National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Yu Tian Road 500, Shanghai 200083, China

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ABSTRACT

The leakage current mechanism of ferroelectric copolymer of polyvinylidene fluoride with trifluoroethylene prepared by Langmuir–Blodgett was investigated in the temperature range from 100 K to 350 K. The electron as the dominant injected carrier was observed in the ferroelectric copolymer films. The transport mechanisms in copolymer strongly depend on the temperature and applied voltage. From 100 K to 200 K, Schottky emission dominates the conduction. With temperature increasing, the Frenkel–Poole emission instead of the Schottky emission to conduct the carrier transport. When the temperature gets to 260 K, the leakage current becomes independent of temperature, and the space charge limited current conduction was observed.

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1. Introduction

The ferroelectric copolymer of polyvinylidene fluoride (PVDF) with trifluoroethylene (TrFE), P(VDF–TrFE), is a candidate material for diversified applications, such as nonvolatile organic memory, piezoelectric sensor, pyroelectric infrared detection, and transducer [1–5]. Polarization fatigue, which means a degradation of the observed polarization with repeated cycling of the applied electric field, is the major impediment for ferroelectric thin films in the applications of nonvolatile memories. Polarization fatigue is a well studied phenomenon in inorganic ferroelectrics, such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ [6,7]. It is believed that polarization fatigue associates with the charge injection from the electrodes into the ferroelectric films [8,9]. So it is important to comprehensively understand the charge injection and transport mechanisms in the ferroelectric thin films during the fatigue process. It was reported that ohmic behavior at lower voltage and Schottky emission or Frenkel–Poole mechanism at higher voltage were observed in $(\text{Ba}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$ thin films [7]. Similar transport mechanisms were also observed in BaTiO_3 thin films [10]. The polarization fatigue of P(VDF–TrFE) thin films have been investigated by several researchers and the charge injection mechanism was also proposed to explain the fatigue. E.g., Xia et al. and Xiao et al. reported

that charge injection in P(VDF–TrFE) was interface-controlled and a Schottky barrier forms at the metal–polymer interface [11,12]. However, the charge transport and the role of charge injection in the fatigue process has not been thoroughly characterized in the ferroelectric polymer of P(VDF–TrFE) [13,14]. E.g., both of them proposed the conduction mechanism based on the data derived from a fixed temperature, i.e., room temperature. More information about the fatigue mechanism can be obtained by investigating the temperature dependence of the leakage behavior, charge injection and transport in the polymer of P(VDF–TrFE). Therefore, in the present work, we study the detailed leakage current behavior of P(VDF–TrFE) films sandwiched between electrodes with dissimilar work functions, and propose charge transport mechanisms over a broad temperature range.

2. Experimental

Sapphire (0001) substrates were ultrasonically cleaned in acetone, alcohol and de-ionized water for 10 min respectively, and then dried in oxygen atmosphere for 5 min. The Au films with the thickness of ~50 nm were deposited on sapphire substrates as the bottom electrodes for growth of P(VDF–TrFE) films. The films of the 70% vinylidene fluoride with 30% trifluoroethylene, P(VDF–TrFE 70:30), were transferred on Au-coated sapphire substrates by using a horizontal Langmuir–Blodgett (LB) technology as described in detail elsewhere [15]. The thickness of the films is about 70 nm, which is measured by using a variable-angle

* Corresponding authors.

E-mail addresses: jlwang@mail.sitp.ac.cn, 329772635@qq.com (J.L. Wang), jlsun@mail.sitp.ac.cn (J.L. Sun).

spectroscopic ellipsometry. Al was evaporated to the P(VDF-TrFE) films through a shadow mask to form the capacitor structure, which was then annealed at 135 °C for 4 h in the air atmosphere to promote the growth of the ferroelectric β -phase. The area of the capacitor was 0.1 mm². The crystal structure of the sample was analyzed by the standard θ - 2θ X-ray diffraction (XRD) method on a Bruker Advanced diffractometer using Cu $K\alpha$ radiation. The polarization vs. electric field (P - E) hysteresis loop was measured using a Radiant Precision LC system. The current-voltage (I - V) curves were conducted by using a Keithley 6430 source meter. The temperature was varied using a computer-controlled cryostat (MMR Tech., Inc.) at a rate of 1 K/min. Since no obvious thermal hysteresis between the heating and cooling processes was observed in the temperature range from 100 K to 350 K, we only show the temperature dependence of the I - V curves of the samples in the cooling process. In order to obtain the intrinsic steady leakage current, the I - V curves are recorded after the initial sweep to remove the influence of the ferroelectric domain switching current.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the LB ferroelectric polymer on the Au electrode. The diffraction peak was observed in the film, $2\theta = 19.97$, which was assigned to the typical (1 10)/(2 00) reflection of the P(VDF-TrFE). Fig. 1(b) demonstrates the hysteresis curve of the samples at room temperature. It can be seen that our P(VDF-TrFE) film shows a saturated hysteresis loop with a remanent polarization (P_r) of $\sim 6.8 \mu\text{C}/\text{cm}^2$ and saturation polarization (P_s) of $\sim 11 \mu\text{C}/\text{cm}^2$ respectively, which indicates good ferroelectricity. It was previously reported that the electron affinity of β -P(VDF-TrFE) was about 4 eV, based on a density functional theory study [16]. The work function value of Au and Al metals are 5.1 eV and 4.1 eV, respectively [17]. The conduction through the lowest unoccupied molecular level (LUMO) of P(VDF-TrFE) and the leakage current is controlled either by the interface energy barrier that exists between the Fermi level of the metal and the LUMO

level of the polymer or by the bulk controlled mechanics such as Frenkel-Poole emission and space charge limited current (SCLC) conduction. The schematic diagram of the band structure of the P(VDF-TrFE) and the work functions of Au and Al are presented in Fig. 1(c). An analogy graph is also presented by Hanna [18]. Fig. 1(d) shows the I - V curve of the P(VDF-TrFE) films measured at 290 K. With the bottom electrode Au as reference, the voltage is swept in a closed loop: from 0 V to -16 V, from -16 V to 16 V, and finally from 16 V back to 0 V. During the voltage applied process, the peak of current is corresponding to the domain switching of ferroelectric films. In order to obtain the intrinsic leakage current, the contribution of the ferroelectric domain switching to the current is eliminated. Fig. 1(d) shows that the leakage current measured with negative biased was clearly higher than that with the positive biased. The result indicate that an n-type transport behavior governs the conduction in our P(VDF-TrFE) films, and the electrons are the dominant type of injected charges, which is consistent with previous report of the leakage conduction type for P(VDF-TrFE) films [18,19].

The temperature dependence of the I - V behaviors from 100 K to 350 K was measured and the temperature dependence of the current density under the voltage 5 V (about 70 MV/m) is presented in Fig. 2(a). It can be seen that the current density increased with the temperature increasing from 100 K to 260 K, but it is nearly independent of temperature as the temperature is higher than 260 K.

It has been reported that the Schottky emission was the dominant leakage current mechanism in the ferroelectric films. Is this mechanism appreciate for the P(VDF-TrFE) films? To address this question, we analyze the temperature dependence of Schottky-limited conduction current density, which can be expressed as [20]:

$$J = AT^2 \exp \left[\frac{-q(\varphi_B - \sqrt{qE/4\pi\epsilon})}{kT} \right] \quad (1)$$

where J is the current density, A is Richardson's constant, T is the absolute temperature, φ_B is the inject barrier height, k is the

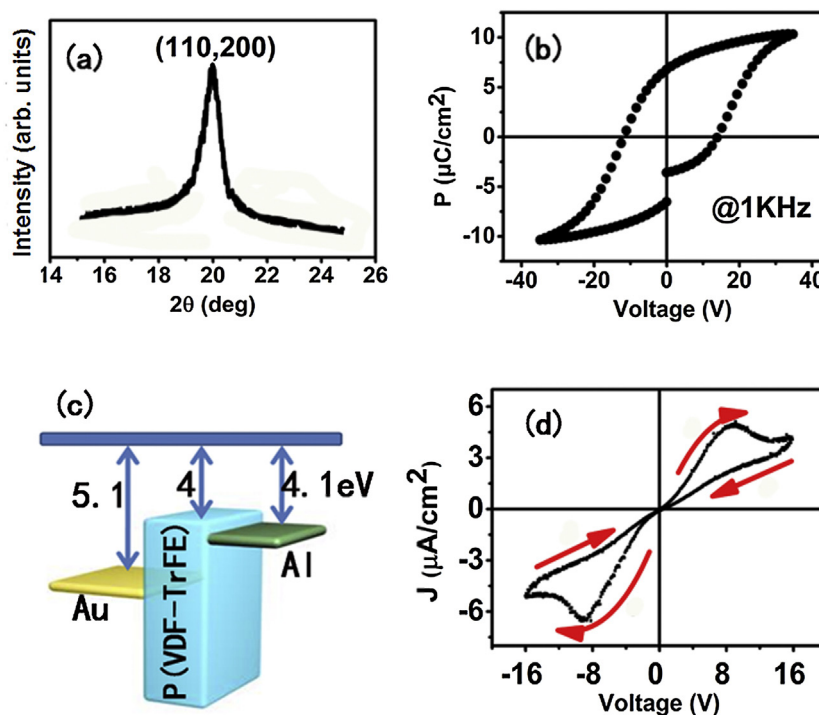


Fig. 1. (a) The XRD pattern of the P(VDF-TrFE) films. (b) The P - V loop for the polymer films at 1 kHz. (c) The schematic of energy band diagram of Au/P(VDF-TrFE)/Al structure. (d) The current density-voltage curve for the P(VDF-TrFE) film at 290 K.

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