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Asymmetric capacitance-voltage curves induced by pinned interface dipoles in poly(vinylidene fluoride/trifluoroethylene) capacitor

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Abstract: The capacitance-voltage (*C-V*) curves of Au/P(VDF-TrFE)/Al capacitor were investigated from 200 K to 310 K. An asymmetry of capacitance value at 0 bias voltage under two polarization orientations was observed at room temperature region, which can be applied in the field of non-volatile memory. The capacitance asymmetry decays with reduced temperature and disappears as the temperature is below 230 K. The phenomena is attributed to a pinned dipole layer between P(VDF-TrFE) films and Al metal electrode.

Key words: P(VDF-TrFE), capacitor, memory, domain walls
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界面极化层引起 P(VDF-TrFE)电容器的电容-电压的不对称

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摘要:通过研究 Au/P(VDF-TrFE)/Al 电容器的变温(200 K 到 310 K)电容-电压曲线,室温下观察到两个极化方向下的电容不对称,这个现象可以应用于非挥发性存储器.电容不对称程度随着温度的降低而变小,当温度低于 230 K,电容不对称现象消失.P(VDF-TrFE)与 Al 电极之间的界面极化层可以解释观察到的电容不对称现象.

关 键 词:P(VDF-TrFE);电容器;存储;畴壁
中图分类号:O469 **文献标识码**:A

Introduction

Poly(vinylidene fluoride/trifluoroethylene) (P(VDF-TrFE)) copolymers are typical ferroelectrics and have attracted great attention for their good ferroelectricity and some unique features, like flexibility and self-healing.[1-4] The P(VDF-TrFE) thin films are considered as interesting candidates for development of many electronic devices such as smart labels, rollable displays, contactless identification transponders, and actuators in Braille displays.[5-8] Most of these applications require a metal/ferroelectric/metal (MFM) capacitor structure to collect signal electrically. Aluminum (Al) is a usual metal electrode in organic ferroelectric capacitor and has been researched extensively.[9-18] Between P(VDF-TrFE) films and Al metal, an interface layer (2 ~ 2.5 nm thick) exists and has a big influence on the properties of the thin P(VDF-TrFE) films, such as a tilt of the polarization-electric (*P-E*) hysteresis loop,[19] a smaller rem-

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nant polarization,[10] a slower domain switching process,[10] and a decrease of permittivity.[10,16-17] Based on dielectric measurements,[16-17] Takahashi and Kitahama considered that an interface associated with nonpolar amorphous phase exists between the organic films and Al metal. However, from the pyroelectric response measurements, Zhao *et. al.*[9] suggested an pinned dipole layer locates at the interface and the pinned dipole points out (up for bottom electrode, down for top electrode) perpendicular to the Al electrode. They attributed the dipole layer to the AlF_3 which may form close to the Al metal during the annealing process. Indeed, AlF_3 was directly observed experimentally between P(VDF-TrFE) and Al metal,[14-15] while no chemical reaction was found when the metals were silver (Ag), gold (Au), and copper (Cu).[15] An asymmetry of polarization state between the two orientations (up and down) is expected if the dipole layer exists only at one side of the MFM structure. To check the potential effect of the polar interface layer between P(VDF-TrFE) films and Al metal, here we investigated capacitance-voltage (*C-V*) curves of the Au/P(VDF-TrFE)/Al capacitors from 200 K to 310 K.

1 Experiments

Copolymer of P(VDF-TrFE) with VDF/TrFE molar ratio of 70/30 was first dissolved in dimethylformamide to form a dilute solution (0.01 wt %) for LB transfer. A horizontal LB technology (Nima 611) was used to transfer 35 layers of P(VDF-TrFE) films on Au-coated Si substrate. The thickness is about 70 nm.[11] Then the as-grown films were annealed at 135℃ for 4h in the air atmosphere to improve the crystallinity. Al was evaporated to the P(VDF-TrFE) films to form the capacitor structures. The *C-V* relationships were measured by using a HP4194A impedance/gain analyzer from 200 K to 310 K. The temperature of the samples was controlled with a cryostat (MMR Tech., Inc.) and varied at a rate of 1 K/min.

2 Results

The capacitance was measured with a static triangular bias voltage wave (-20 V to 20 V, then back to -20 V) applying to the top Al electrode while the bottom Au electrode was grounded (inset of Fig. 1). The bias voltage dependence of the capacitance and dielectric loss (tanδ) of Au/P(VDF-TrFE)/Al capacitor at 310 K is displayed in Fig. 1. Both the *C-V* curves and the tanδ-V curves have the characteristic butterfly shape with two maxima of the capacitance, indicating the switching of the polarization at the coercive voltage $V_c \sim \pm 6$ V. Considering the thickness of ~70 nm, the coercive field (E_c) is ~85 MV/m, which agrees well with other reports.[10-11,13,20] Note that an additional peak (shoulder) appears near 0 bias voltage in both *C-V* curves and tanδ-V curves when the voltage sweeps from -20 V to 20 V, resulting in an asymmetry of capacitance value at 0 bias voltage in the two polarization orientations. The two switchable capacitance states can be read out with a small electric signal, which can be used in the field of non-volatile memories.

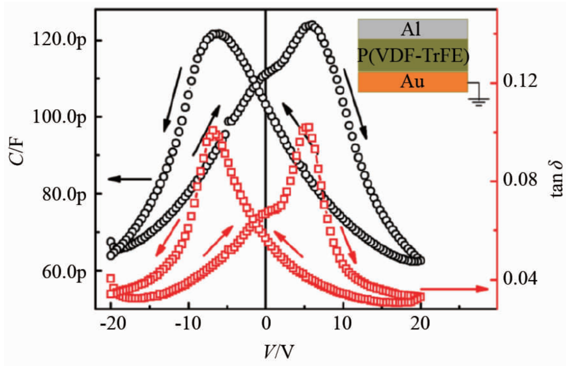

Fig. 1 *C-V* curves (left) and dielectric loss- *V* (right) at room temperature. Inset shows the side sketch of the Au/P(VDF-TrFE)/Al capacitor

图1 室温下的 *C-V* 曲线(左)和介电损耗-电压曲线(右). 插图中显示 Au/P(VDF-TrFE)/Al 电容器结构

The *C-V* curves were further performed from 200 K to 310 K. Figure 2(a) shows the *C-V* curves at 300 K, 260 K and 220 K, respectively. The capacitance shoulder near 0 bias voltage decays with the decrease of temperature. The difference of capacitance between the two polarization states almost disappears when the temperature is below 230 K (Fig. 2(b)). Here we defined "C_{up}" and "C_{down}" as the capacitance when polarization points up (top Al electrode) and down (bottom Au electrode), respectively. The temperature dependence of capacitance asymmetry ratio [(C_{up}-C_{down})/C_{up}, %] at 0 bias voltage is shown in Fig. 2(b) (right). The capacitance asymmetry ratio is very weak (less than 2%) at low temperature region (below 230 K), begins to increase at 240 K, and is stable (~4%) from 250 K to 290 K. However, the asymmetry ratio increases again as the temperature is higher than 300 K. It is around 5% at room temperature and higher value is expected in higher temperature region (higher than room temperature and below than phase transition temperature, i. e., ~380 K). The poor temperature stability is a drawback for its application in non-volatile memories. To improve the temperature stability, understanding the physical origin of the asymmetry phenomena is crucial.

3 Disscussions

The capacitance (C) is determined by $C = \frac{\varepsilon_0 \varepsilon_{eff} S}{l}$, where ε_0, ε_{eff}, S and l are the vacuum permittivity, the effective permittivity of the films, the area of the electrode and the thickness of the films, respectively. The capacitance asymmetry is attributed to the different manner of ε_{eff} between the two polarization states since other parameters ε_0, S, and l are constants. As aforementioned, an interface layer exists between the P(VDF-TrFE) films and Al metal. The impact of the interface layer on the ε_{eff} can be described by the well-known in-series capacitor formula[10, 17]:

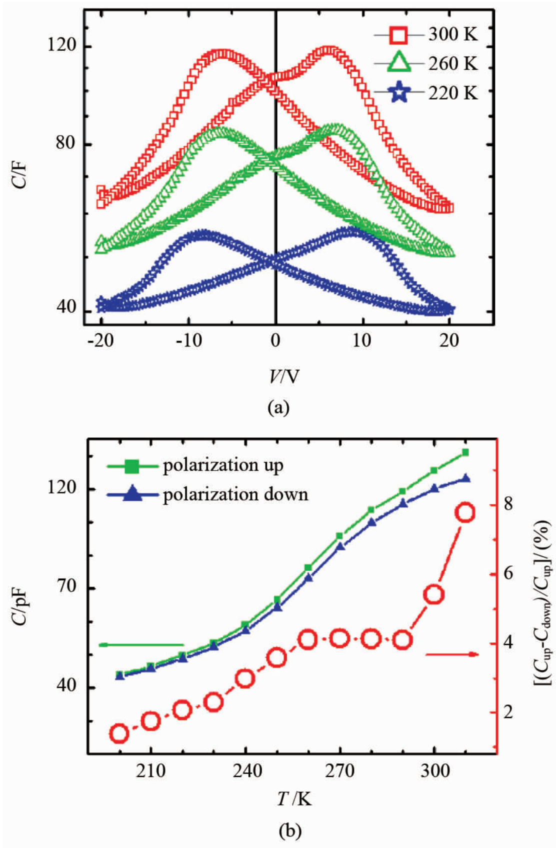

Fig. 2　(a) The C-V curves at 300 K, 260 K and 220 K, respectively, (b) The temperature dependence of capacitance and capacitance asymmetry ratio at 0 bias voltage (right) between two polarization orientations
图 2　(a) 300 K, 260 K 和 220 K 温度下的 C-V 曲线, (b) 两个极化状态下的电容变温曲线(左)和零偏压下电容不对称比率(右)

$$\frac{l}{\varepsilon_{\mathrm{eff}}}=\frac{d}{\varepsilon_f}+\frac{\delta}{\varepsilon_\delta}\quad,\quad(1)$$

where $l=d+\delta$, ε_f and d are the permittivity and thickness of the ferroelectric, and ε_δ and δ are the permittivity and thickness of the interface layer, respectively. From Eq. 1, ε_f and ε_δ can affect the $\varepsilon_{\mathrm{eff}}$ in the same way. Considering that $d \gg \delta$ ($d\sim70$ nm and $\delta\sim2$ nm), it is ε_f that plays a crucial role for the asymmetric phenomena observed in those experiments. ε_f is controlled by two parts[10]: the lattice contribution and the contribution of domain walls. Domain walls will also increase tanδ by generating heat. This is why both C-V and tanδ-V curves show a maximum at the coercive voltage when many domain walls move because of the polarization switching (Fig. 1).

For Au/P(VDF-TrFE)/Al capacitors, the presence of the interface layer leads to a depolarizing field (E_d). Gysel *et al.*[10] suggested that when reducing the applied field, the magnitude of the E_d will induce the back switching of the polarization, which leads to the formation of multi domains from the single-domain state. This can explain the capacitance shoulder appeared in C-V and tanδ-V curves when sweeping the bias voltage from -20 V to 20 V (Fig. 1). Note that this capacitance shoulder is absent when sweeping the bias voltage from 20 V to -20 V. This can be easily understood considering that AlF_3 at the Al metal side leads to a pinned interface layer with dipole pointing down perpendicular to the Al top electrode. As analyzed below, E_d in polarization down state ($E_{d\text{-down}}$) is much smaller than that in polarization up state ($E_{d\text{-up}}$). The $E_{d\text{-down}}$ is smaller than E_c and cannot break the single-domain state while the $E_{d\text{-up}}$ is larger than E_c and back-switches the up polarization leading to the multi domains state (capacitance shoulder in C-V curves).

The energy potential profiles of the capacitor under the polarization up and down states are shown in Fig. 3 (a) and 3(b), respectively. To be simple, we treated that the pinned dipole layer has a similar band gap and similar polarization as P(VDF-TrFE) films. When the polarization points right/up, as shown in Fig. 3(a), a charge thin slab with positive sign locates at the contact interface between P(VDF-TrFE) films and the pinned dipole layer, leading to a big drop of energy potential at the contact interface[22]. On the contrary, when the polarization is switched to left/down, as shown in Fig. 3 (b), only the imperfect screening of electrode gives a weak shift of energy potential[22-23]. A remarkable gradient of the energy potential in the polarization right/up state gives a higher $E_{d\text{-up}}$ and destabilizes the single-domain, while a weak gradient of the energy potential in the polarization left/down state results in a small $E_{d\text{-down}}$ which has little effect on the single-domain state. That is why that the capacitance shoulder is only observed as the bias sweeps from -20 V to 20 V.

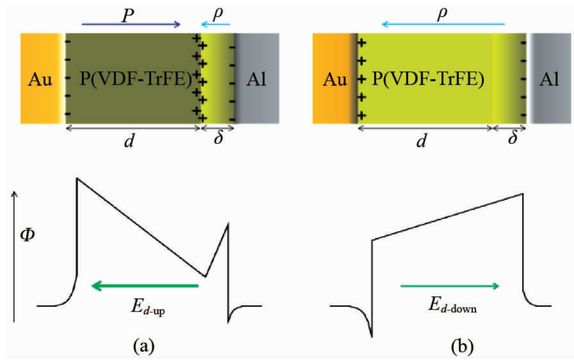

Fig. 3　The energy potential profiles when polarization points to Au electrode (a) or Al electrode (b). Insets show the corresponding sketch of the Au/P(VDF-TrFE)/Al capacitor
图 3　当极化指向金电极(a)或铝电极(b)时的能量势. 插图显示相应的 Au/P(VDF-TrFE)/Al 电容器结构

The temperature dependence of the capacitance asymmetry (Fig. 2b) further confirms our analysis. At low temperatures, where E_c is relatively high, even $E_{d\text{-up}}$ is not strong enough to induce the multi-domain state at $E=0$ (E, electric field)[10]. The characteristic temperature 230K, below which the phenomena almost disappear, is in agree with that reported by Gysel *et al.*[10].

Despite the pinned dipole interface effect, the difference of the work functions of the electrodes should also be considered. The difference of work functions between the top Al electrode (4.3 eV) and bottom Au electrode (5.1 eV) gives a constant built-in electric field (~ 10MV/m) which points to left/down. When the polarization points right/up, the built-in electric field enhances the $E_{d\text{-up}}$, while when the polarization points left/down, the built-in electric field weakens the $E_{d\text{-down}}$. This built-in electric field has a similar effect with the pinned dipole interface and can also contribute to the phenomena observed in this experiment.

4 Conclusions

A capacitance shoulder in C-V curves (when bias voltage sweeps from -20 V to 20 V) have been observed in the Au/P(VDF-TrFE)/Al capacitor. The capacitance shoulder decreases with the decrease of temperature. This can be explained by asymmetric E_d ($E_{d\text{-up}} \gg E_{d\text{-down}}$) because of the interface pinned dipoles at Al electrode side and the difference of work functions between the top Al electrode and bottom Au electrode. The large $E_{d\text{-up}}$ breaks the up single domain to multi domains state while the small $E_{d\text{-down}}$ has little effect on down single domain, which leads to $C_{up} > C_{down}$ at 0 bias voltage. This asymmetric of capacitance suggests a potential application in the field of non-volatile memories.

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