Abstract

The carrier motion mechanism in capacitors with ferroelectric poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] film was investigated in terms of displacement current analysis. The coercive electric field of the ferroelectric polymer was measured by applying a ramp voltage on an IZO/P(VDF-TrFE)/Au structure (MFM structure) with a value about 0.7 MV/cm. Subsequently, by introducing a pentacene layer to the MFM structure, namely the IZO/P(VDF-TrFE)/Pentacene/Au structure (MFSM structure) we studied carrier injection and accumulation process in the pentacene semiconductor layer under the effect of dipole reversal in the ferroelectric layer. Interestingly, three peaks were found for the MFSM structure and they were understood by taking into account charge motion in pentacene layer. The present study shows displacement current measurement is a useful technique to detect carrier motion in organic devices.

Keywords: ferroelectric; polarization; displacement current; carrier injection

1. Introduction

Organic ferroelectrics have been intensively studied for decades because of their unique properties [1]. Among them, the poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer is of special interest owing to its strong ferroelectric property [2] and potential applications in electronics such as nonvolatile memory elements, ultrasonic transducers and sensors [1,3]. Its ferroelectricity originates from the molecular dipoles associated with positively charged hydrogen atoms and negatively charged fluorine atoms attached perpendicular to the chain axes. It has been reported that thin films prepared by spin-coating method consist of relatively large crystalline grains and that the molecular chain axes are aligned parallel to the film surface [4]. The all-trans conformation of chain molecules and their parallel packing induce the alignment of all molecular dipoles in one direction to produce a large spontaneous polarization, which is important for the above-mentioned applications [5].

On the other hand, since the discovery of high-mobility organic semiconductors, organic electronic devices have attracted comprehensive interest owing to their unique advantages, such as mechanical flexibility, light weight, low-temperature process, and especially their low cost [6]. It is well known that organic electronic devices are basically...
injection-type devices owing to the low intrinsic carrier density, where most of the carriers in the organic active layer are injected from the metal electrode \cite{7}. Thus, clarification of the carrier injection property from the metal electrode to the organic semiconductor is crucial \cite{8}. Along with the discovery of organic semiconductors, organic insulating materials have also been highly developed. Among them PVDF and related copolymers are important material used as gate insulators \cite{6,9} as well as an interlayer between the active layer and the inorganic insulator \cite{6,10-12}. Hence it is essential to understand carrier motion in organic semiconductors in combination with PVDF insulators, such as in a double-layer structure. In our recent studies, we applied a similar ferroelectric layer, P(VDF-TrFE), to an organic field-effect transistor (OFET) structure as a gate insulator to investigate the carrier injection, accumulation, and transport processes of the OFET device on the basis of dielectric physics and Maxwell-Wagner model \cite{13-15}. Although we found that the spontaneous polarization of the ferroelectric gate insulator modulated the amount of charge that accumulated at the pentacene OFET channel and thus also changed the transfer properties, important details remain unclear owing to the complex structure of the OFET structure. Hence, to avoid the disadvantages of the OFET structure and to clarify the relationship between carrier injection from the metal to the organic semiconductor (such as pentacene) and the spontaneous polarization of P(VDF-TrFE) ferroelectric material, it is crucial to first carefully investigate P(VDF-TrFE) single- and double-layer structures, namely, the metal-ferroelectric-metal (MFM) and metal-ferroelectric-semiconductor-metal (MFSM) structures.

In the present study, in order to clarify the carrier motion in the organic semiconductor under the effect of polarization reversal in ferroelectric layer, we first investigated the polarization reversal of a P(VDF-TrFE) single layer using displacement current measurement (DCM) and then studied how the polarization reversal in P(VDF-TrFE) influences carrier injection into the pentacene layer in the structure of Au/pentacene/P(VDF-TrFE)/IZO (indium zinc oxide). The advantage of using double layer structure is that we can analyze the potential built at the interface in terms of carrier behavior in active layers as well as in PVDF layer. The experimental results showed that carrier injection from Au into the pentacene layer was strongly related to polarization reversal in P(VDF-TrFE).

### 2. Experiment

#### 2.1. Sample Preparation

To detect electrical properties of the P(VDF-TrFE) copolymer, an MFM capacitor structure was prepared. Meanwhile to investigate carrier motion under the effect of polarization reversal, we employed the MFSM structure illustrated as Fig. 1. In detail, P(VDF-TrFE) copolymer powder (Daikin Kogyo Co., Ltd.) (molar ratio of 72 : 28 for VDF to TrFE) was first dissolved in methyl-ethyl-ketone solvent (MEK, Sigma-Aldrich company; concentration: 5 wt%). Then the solution was subjected to spin-coating onto a pre-cleaned IZO surface, subsequently annealed in a dry nitrogen atmosphere at 150 °C for 1.5 h, and cooled down to room temperature. The thickness of the spin-coated P(VDF-TrFE) layer was measured to be about 200 nm using a profilometer (DEKTAK3ST). Afterwards, a pentacene layer with a thickness of 200 nm and a subsequent gold top electrode with a thickness of 100 nm were
thermally evaporated on the copolymer layer at a vacuum pressure below $10^{-3}$ Pa. The deposition speeds of pentacene were regulated to 0.7 Å/s using a quartz crystal microbalance (QCM). The designed effective area for each device was approximately 3 mm$^2$.

2.2. Displacement current measurement (DCM)

To study carrier behavior in the capacitors, DCM was employed. In detail, a ramp voltage generated by a function generator (NF, WF 1945) and then amplified with a power amplifier (NF, BA4825) was applied onto the IZO electrode with reference to the Au electrode, as shown in Fig. 1. The amplitude of the ramp voltage for MFM structure capacitor was 40 V, while for MFSM structure capacitor it was 60 V. To make easier comparison, frequencies of ramp voltage for both structures were kept the same of 50 mHz. The current-voltage ($I$-$V$) characteristics were measured using a current meter and a voltage meter, Keithley 6517 and Keithley 2000, respectively.

![Fig. 2: $I$-$V$ characteristics for the single and double-layer capacitors. The inset in (a) is a magnification of the current for a small range of applied voltage. The arrows denote the change direction of the applied voltage.](image)

3. Results of DCM

Figure 2 shows the $I$-$V$ characteristics for the MFM and MFSM capacitor structures. Two peaks with nearly symmetric peak position as well as peak height were clearly observed for single layer capacitor structure as illustrated in Fig. 2(a), which indicates there is a dipole reversal process at the peak voltage. Interestingly, for double layer capacitor structures, there are three peaks as shown in Fig. 2(b). Among them, in spite of Peak 3, Peak 1 and Peak 2 have approximately symmetric peak position and if compared with Fig. 2(a) the position is nearly the same as that for single layer structure. Importantly different from single layer case, Peak 1 and Peak 2 have different peak height. These differences indicate there is a carrier-motion process in the double layer structure. For details, we will discuss the origins of all peaks for the two structures below.

4. Discussion on the origins of peaks

4.1. Theoretic analysis

For the MFSM structure as shown in Fig. 3(a), when positive voltage is applied on IZO electrode, positive charge will be induced on the lower electrode (IZO electrode) while negative charge is induced on upper electrode (Au electrode). Suppose the dipole of P(VDF-TrFE) layer is oriented downward, which is opposite to the applied electric field. By considering accumulated charges at the interface with a surface density $Q_s$, the total charge density on the upper and lower electrode surfaces ($Q_1$ and $Q_2$) can be respectively expressed as
where the total capacitance per unit area $C$ is regarded as the total capacitance density of Layer 1 of pentacene and Layer 2 of P(VDF-TrFE) in series, namely, $C = C_1 C_2 / (C_1 + C_2)$, and $P$ is the remanent polarization of Layer 2. The first term of both equations represents the charge generated by the applied external voltage, and the other terms are the charge induced on the electrode surface due to the presence of interface charge and polarization of the P(VDF-TrFE) layer. Note that the equations must satisfy the charge neutrality condition in the device: $Q_1 + Q_2 + Q_3 = 0$. The total current flowing through the device is composed of two parts: displacement current and conduction current. Considering the conduction current through Layer 1 ($I_1$) and Layer 2 ($I_2$), the continuous current at the electrodes

$$I = (-\frac{\partial Q_1}{\partial t} + j_{c1})S = (\frac{\partial Q_2}{\partial t} + j_{c2})S,$$

yields the current measured by an ammeter as

where $j_{c1}$ and $j_{c2}$ are the conduction current densities in Layer 1 and Layer 2, respectively, and $S$ is the effective area of the device. Note that the eq. (3) satisfies the current continuity of $\frac{\partial Q_s}{\partial t} = j_{c1} - j_{c2}$ at the interface. By substituting $Q_2$ in eq. (2) for that in eq. (3), the current is obtained as

under the assumption of negligible leakage current through the P(VDF-TrFE) insulator layer ($j_{c2} = 0$). In our displacement current measurements, the first term $C_1 V / \partial t$ is a constant that equals to $-4fCV_0$ or $4fCV_0$, where $f$ and $V_0$ are frequency and amplitude of the applied voltage, respectively. From the second and third terms of eq. (4), we

$$I = (C_1 \frac{\partial V}{\partial t} - \frac{\partial Q_1}{\partial t} \frac{C_2}{C_1 + C_2} - \frac{\partial P}{\partial t} \frac{C_1}{C_1 + C_2})S,$$

can predict that the change of $Q_s$ or $P$ will result in change of current measured by the ampere meter.

Fig. 3: Sketches of the MFSM structure for DCM analysis. The current directions in the figures are the reference direction. (a) At forward bias, dipole is oriented downward and the accumulated holes at the interface are about to return to the upper electrode (as the dotted arrow illustrated), which corresponds to the situation just before Peak 2 (in Fig. 2(b)) occurs; (b) at backward bias, dipole is oriented upward and holes are about to inject into pentacene layer (as the dotted arrow illustrated), which corresponds to the situation just before Peak 1 (in Fig. 2(b)) occurs.

4.2. MFM structure capacitor
For MIM structure, there is no interface for accumulating charges, so we just consider $Q_s = 0$ in eq. (4). Therefore, the appearance of one peak at a certain applied voltage is only due to the change in polarization $P$, which indicates the presence of polarization reversal. From the peak positions, we can calculate the coercive electric field ($E_c$) to be approximately 0.7 MV/cm, which is in agreement with a commonly reported value $^{[16,17]}$. Note that the peak positions for two peaks are actually non symmetric but with a small discrimination of around 0.6 V, which is probably due to the work function difference between the top electrode of Au and the bottom electrode of IZO. Actually, in general IZO has a slightly lower Fermi energy level ($4.5$ eV $^{[18]}$) than Au ($5.1$ eV $^{[19,20]}$). In addition, the displacement current under the condition of $V = 0$, shown in the inset of Fig. 2(a) almost agrees with the calculated values from eq. (4) using a relative dielectric constant of 10 for the P(VDF-TrFE) layer $^{[21,22]}$, a working area of 3 mm$^2$, and a layer thickness of 200 nm, i.e., the experimental values. If we integrate the peak area in the current-time (I-t) plot (not shown here), we can find the areas of two presented peaks are same, which indicates the induced charges corresponding to polarization reversal are in equilibrium at backward and forward biases.

4.3. MFSM structure capacitor

Different from MFM structure in which the voltage across the P(VDF-TrFE) layer is always simply equal to the applied voltage, MFSM structure is more complex in voltage contribution due to charge injection and accumulation at the interface of the double layers. In the following section, we will analyze the charge motion responsible for the diverse $I$-$V$ characteristics in MFSM structure.

A. In region $V < 0$

It is known that holes can inject from Au into pentacene very smoothly. Hence in our case, backward bias will possibly induce hole injection into pentacene layer. However, owing to the existence of dipole layer which yields an electric field in pentacene opposing to the applied electric field as illustrated in Fig. 3(b), the hole injection cannot happen until the applied electric field could cancel out the effect of dipole layer. Once holes are injected into pentacene layer and accumulate at the interface of P(VDF-TrFE)/pentance, we can consider pentacene layer as a conductive material, and then all the applied voltage is just across on the P(VDF-TrFE) layer. The situation is somewhat like that in an MFM structure, so it is reasonable that the peak position is the same of -14 V as that for single layer structure as shown in Fig. 2(a). Therefore, we claim Peak 1 corresponds to hole injection (see Fig. 3 (b)) and dipole reversal simultaneously. In addition, according to eq. (4), if accumulated charge density changes from 0 to $Q_s$ and the polarization charge density changes from $-P$ to $P$, the current will get a negative maximum, which is demonstrated by the appearance of the highest peak of Peak 1, whose area in I-t plot is the sum of Peak 2 and 3 (not shown here).

B. In region $V > 0$

As the voltage increases to -60 V and then decreases to zero, the dipole remains its orientation and the accumulated holes also remain at the interface, which is just as Fig. 3(a) illustrated. When voltage becomes forward bias, as the external electric field increased and cancels out the electric field induced by dipole of P(VDF-TrFE), the accumulated holes are repelled to Au electrode and neutralized the negative charge at Au electrode induced by applied voltage (see Fig. 3(a)). Position of Peak 2 just corresponds to the potential that satisfies $Q_1 = 0$. Then the applied voltage attributes to double layers. So the coercive electric field of P(VDF-TrFE) could be reached at a larger voltage, namely the voltage of Peak 3. Therefore, it is polarization reversal that is responsible for Peak 3. To be sure, the assigned origins for the Peak 2 and 3 still need more proof, which is our future task by using technique of second harmonic generation to detect carrier motion in the device $^{[23]}$. In addition, according to eq. (4), when accumulated charge density changes from $Q_s$ to 0 (corresponds to Peak 2), or the polarization charge density changes from $P$ to $-P$ (corresponds to Peak 3), the current will both get a positive maximum, as demonstrated by the appearances of Peak 2 and Peak 3. Note that the voltage amplitude of Peak 1 is slightly larger than that of Peak 2, the divergence between them is ascribed to a very small energy barrier for holes injected into pentacene layer.

5. Conclusions

We studied the carrier behavior in capacitors with a ferroelectric P(VDF-TrFE) copolymer layer by analyzing the displacement current. By contrast to the $I$-$V$ characteristics of MFM capacitor structure and considering hole
injection, we accounted for the three peaks generated in MFSM capacitor structure as: Peak 1 was ascribed to dipole reversal and holes injection into pentacene layer at the same time; Peak 2 corresponded to the injected holes being repelled to Au electrode; Peak 3 reflected dipole reversal. Thus, the study shows DCM is a useful method to investigate the carrier motion in the ferroelectric capacitors.

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