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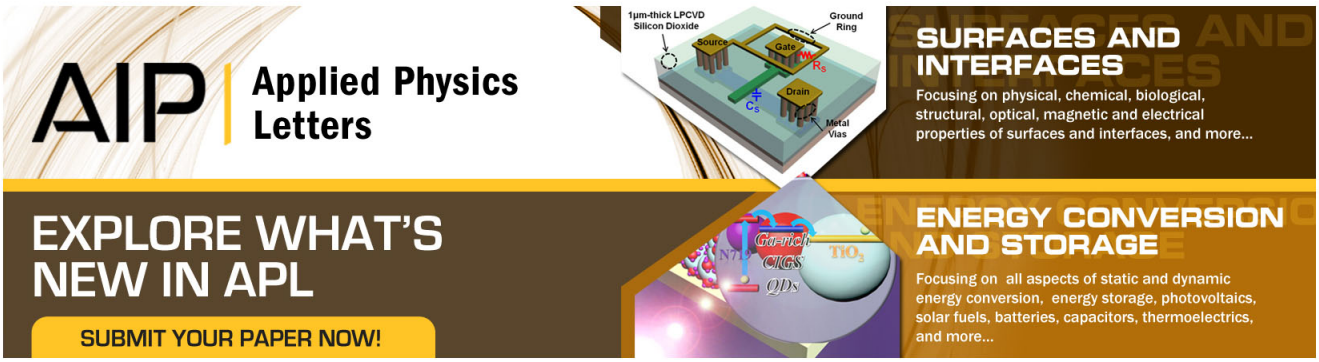

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Local surface potential distribution and its relaxation in ferroelectric poly(vinylidenefluoride-co-trifluoroethylene) thin films

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Local surface potential distributions and their relaxation behavior in ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) thin films were investigated using Kelvin-probe force microscopy. All surface potentials were negative regardless of the sign of the applied voltage because of the intrinsic negative charges that originated from the self-aligned region of dipoles at the ferroelectric/electrode interface. Importantly, the intrinsic charges would have a remarkable influence on the reliability of written data. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4734870]

Poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] copolymers have recently attracted attention for their emerging applications including non-volatile memories, tactile sensors, and energy harvesters because of their relatively large remnant polarization, short response time, and compatibility with conventional complementary metal-oxide semiconductor (CMOS) technology.[1–4] Advantages, such as low crystallization temperature ($<150\,^{\circ}C$), low-cost solution processing, and chemical stability, make ferroelectric copolymers a leading candidate for organic and flexible electronics. Importantly, the investigation of ferroelectric switching in P(VDF–TrFE) ultrathin film has generated enormous interest in the scaling behavior of the copolymers and their efficacy in non-volatile memories.[5–9] The spontaneous polarization in ferroelectric materials can be reversibly switched between two states by applying an external electric field and thus the bistable polarization at zero bias is used to represent two different data bits corresponding to 0 and 1 states in the memory devices. In order to study the static and dynamic properties of ferroelectric organic films at the nanoscale level, piezoresponse force microscopy (PFM), which relies on the detection of piezoelectric vibrations induced by the application of a weak ac voltage to the conducting tip in the contact mode, has been recently adopted.[7–10] For example, Kim *et al*. investigated the nanoscale domain growth dynamics of the bistable polarization in the P(VDF-TrFE) thin film.[8] Park *et al*. quantitatively assessed the preferentially aligned polarizations in the as-received films.[10] In the PFM measurements, the amount of piezoelectric vibrations reflecting local effective piezoelectric coefficients can be measure of local charge at the surface but it is also related to permittivity and elastic compliance. Meanwhile, Kelvin-probe force microscopy (KFM) has been developed as a nondestructive way to image potential distributions on the surface and to characterize the electrical properties of ferroelectric domains.[11] KFM is contact-less and thus it is very suitable for studies of both soft organic and biological samples in comparison to PFM. To date, KFM has been utilized to map surface potential profiles in ferroelectric oxide films.[12–15] It is crucial to understand the surface potential distribution and its relaxation on differently poled regions since this understanding directly pertains to bit signals and reliability for memory and data-storage applications. Unfortunately, a progressive loss of remnant polarization (referred as retention loss) in ferroelectric organic films has not been well studied, yet. In this study, we report time-resolved surface potential analysis in P(VDF-TrFE) thin films in order to understand their retention loss.

Procedures for the fabrication of P(VDF-TrFE) thin films are described in detail elsewhere.[16] The thickness of the sample is 90 nm. KFM measurements were conducted using a commercial atomic force microscope (AFM, SPA400, Seiko Inc.) with a Pt-coated conductive tip (EFM-50, Nanoworld). Since adsorbed water molecules can have an influence on the surface potential in KFM imaging due to their dipole moments, the relative humidity in the KFM chamber was thoroughly kept below 15% using humidity control agents. Initially, a writing step was performed by various scanning area with different voltages applied to the bottom electrode over a scan area of $5 \times 5\,\mu$m in contact-mode AFM. Subsequently, a reading step was carried out by scanning $2 \times 2\,\mu$m area with an ac modulation voltage of 10 V with a frequency of 25 kHz in non-contact mode KFM. The surface potential relaxation was investigated by the change in surface potentials over time.

Figure 1 shows surface potential images of the poled regions on the sample with different voltages applied to the bottom electrode. Figure 2 is the average surface potential, which was obtained from the entire image, as a function of time for each applied voltage. The surface potential shows exponentially decaying relaxation behaviors. The surface potential changed at a faster rate during the initial stage of relaxation (until 60 min) due to the spread of the surface charges, then the decaying rate slowed and the surface potential became stable. The solid line below surface potential values denotes the decaying exponential, $y = y_0 + A\exp\left(-\frac{t}{\tau}\right)$, where y_0 is the offset of each decaying curve, A is the physical magnitude of the initial state, and τ is the relaxation time. Table I summarizes the fitted values. Interestingly, the spread of the surface charges in the positively written area was faster than that in the negatively written area.

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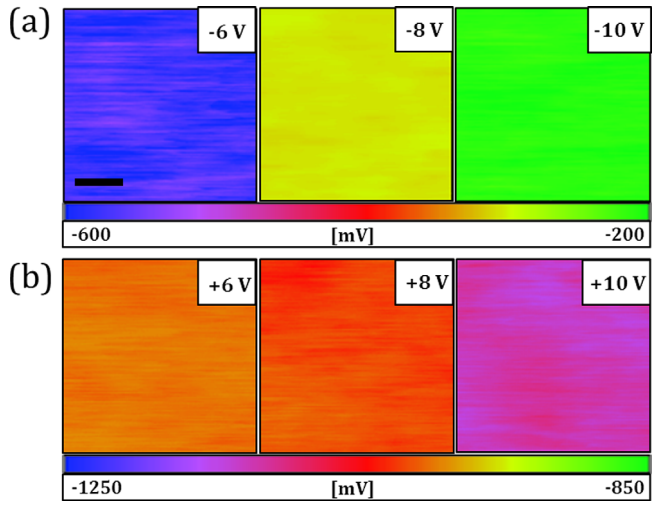

FIG. 1. Surface potential distribution of poled regions with different voltages of (a) −6, −8, and −10 V, and (b) +6, +8, and +10 V applied to the bottom electrode, respectively.

It is worth noting that all surface potentials on P(VDF-TrFE) thin films have negative values regardless of the sign of the applied voltage. The absolute value of the initial surface potential under the application of a positive writing voltage was higher than that under the application of a negative writing voltage. We also obtained the surface potential image of the bare state region, which was not poled by an applying voltage but scanned by an electrically grounded tip for desired times (Figure S1).[17] When the electrically grounded tip is scanned by the contact mode, mobile screen charges on the P(VDF-TrFE) surface will be swept to the tip because of the potential difference between the tip and the surface screen charge. This is referred as screen charge transfer.[18] The average surface potential at bare state was −738.8 mV. Even after the scans were repeated once and three times, the average surface potentials were not significantly changed (i.e., they were −737.5 and −734.5 mV, respectively). We think that this would result from the intrinsic negative charges that are originated from downward self-aligned region of dipoles in the vicinity of the bottom electrode. As-received P(VDF-TrFE) thin films showed uniform dark contrast in the phase image during PFM imaging (Figure S2).[17] This implies that electric dipoles in the virgin state were self-aligned region of dipoles in the direction from surface to the bottom electrode. It should be noted that the self-aligned region of dipoles without external poling in spin-coated P(VDF-TrFE) thin films have been reported elsewhere.[9,10] Additionally, we observed significant shift of the piezoresponse hysteresis loop along the voltage axis in our films, which indicates another clue of the self-aligned region of dipoles near the bottom electrode (Figure S3).[17] Unlike inorganic materials, ferroelectric polymers consist of amorphous and one (or more) crystalline phases in which polymer chains are differently packed. Their polarization reversal results from the rotation of molecules about their chain axes. For the downward ferroelectric polarization, hydrogen cations (H^+) provide attractive interaction with Au surface and fluorine anions (F^-) are abundant near film surface. The polarization switching is performed by a nucleation process such that H^+ detaches from the Au surface with an external electric field strong enough. Accordingly, we think that this negatively asymmetric surface potential behavior would arise from the presence of the internal built-in field near the ferroelectric/electrode interface. When there is an internal built-in field near the ferroelectric/electrode interface, this field does not depend on the external applied voltage and always aligns in one direction. Finally, the built-in field generates a self-aligned region of dipoles near the ferroelectric/electrode interface.

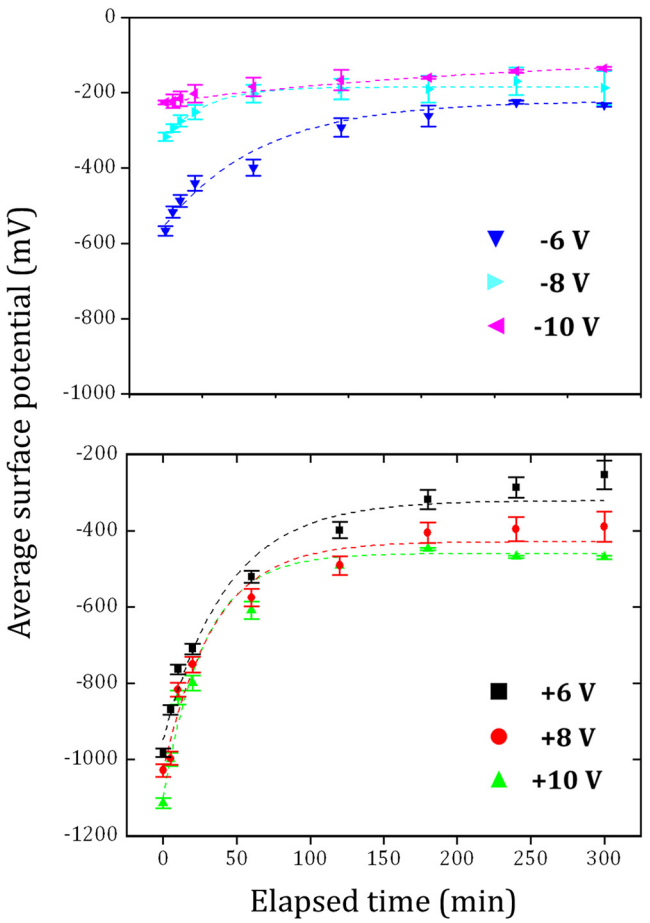

FIG. 2. Average surface potential values of differently poled regions as a function of the elapsed time.

TABLE I. Fitted values for time evolution of the surface potential on the P(VDF-TrFE) film.

Writing voltage	−10 V	−8 V	−6 V	+6 V	+8 V	+10 V
y_0	−129.4	−183.2	−218.9	−280.2	−410.9	−471.4
A	−92.5	−130.2	−319.3	−644.3	−603.7	−607.1
τ	127.8	105.2	83.3	57.7	40.8	31.2

For further understanding of the origin of the surface potential, we described surface charge species consisting of polarization, screen and internal charges on the basis of the following assumptions: (a) Internal negative charges from the self-aligned region of dipoles always stay underneath the film surface even when a voltage with opposite sign is applied to the bottom electrode. (b) The amount of polarization charge changes depending on the writing voltage.

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(c) The amount of charges injected from the conductive probe onto the sample surface is linearly proportional to the applied voltage. Importantly, when a positive (negative) voltage pulse above the coercive field is applied to the bottom electrode, the upward (downward) polarization is induced and negative (positive) charges are simultaneously injected from the tip into the sample where they are trapped on the surface. Meanwhile, the polarization may induce space-charges in amorphous phases. The total amount of measurable charges via KFM can be expressed as

$$C_{Total} = C_S + C_P + \ C_I, \tag{1}$$

where C_S is intrinsic charges from the self-aligned region of dipoles, C_P is induced charges by permanent electric dipoles, and C_I is injected charges from the tip. Although C_S is always negative in this study, both C_P and C_I are negative when a positive voltage (above coercive voltage) is applied to the bottom electrode, and vice versa. Interestingly, the effect of the intrinsic charges is much stronger than that of both induced and injected charges in ultrathin films and thus negative surface potential regardless of the sign of the applied voltages can be expected. This coincides with our observations (Figure 2). Furthermore, the downward polarization in the self-aligned region of dipoles would have a significant influence on the relaxation of the surface charges since it makes the induced upward polarization be more unstable than the induced downward polarization.

In summary, we investigated the local surface potential distribution and its relaxation behavior in P(VDF-TrFE) ultrathin films using the KFM. All surface potentials were negative regardless of the sign of the applied voltage because of the intrinsic negative charges that originated from the self-aligned region of dipoles at the ferroelectric/electrode interface. The intrinsic charges in the P(VDF-TrFE) films would have a remarkable influence on the reliability of written data. Based on this observation, we are currently exploring the performance of nonvolatile ferroelectric memory devices fabricated with self-aligned P(VDF-TrFE) films.

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