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Enhanced Functional and Structural Characteristics of Poly(vinylidene-trifluoroethylene) Copolymer Thin Films by Corona Poling

Chien A. Nguyen, Pooi See Lee, Wu Aik Yee, Xuehong Lu, Madhavi Srinivasan, and Subodh G. Mhaisalkar

Department of Materials Science and Engineering, Nanyang Technological University, Singapore 639798


Poly(vinylidene fluoride) (PVDF) and the copolymer family e.g., P(VDF-TrFE), P(VDF-HFP), P(VDF-TrFE-CtFE), etc. have been studied for ferroelectricity in memory applications, electrostriction, piezoelectricity, as well as electromechanical applications. To enhance the remnant polarization properties, different electrical poling methods have been used, e.g., thermoelectrets and corona poling. The major advantage of corona poling over thermoelectrets is that electrodes are not required on the sample surface subjected to the corona field. This enables the possibility of a noninvasive modification of the film’s crystalline properties and also effectively reduces the likelihood of catastrophic local dielectric breakdown.

Studies of corona poling on ferroelectric copolymers have usually focused on changes in properties of thick (>10 μm thickness) films. Most of these studies have shown enhanced polarization properties with minimal residual charges existing at the top surface of the films subjected to either positive or negative corona poling. Nevertheless, these reports were not accompanied by characteristics of surface morphology and crystalline structure related to the changes in polarization properties. Also, this information has not been available for thin film samples (<1 μm thickness). Due to the presence of trifluoroethylene, P(VDF-TrFE) copolymer films can readily crystallize into a mixture of para- and ferroelectric phases, which exist in rod-like grains at suitable annealing temperature below the melting point. Polarization dipoles in these phases can be reoriented under the corona discharge field during the postprocess. As a result, by simultaneously combining corona poling with thermoelectrets and corona poling methods, we can enhance the ferroelectric properties with minimal residual charges existing at the top surface of the film.

Table I. The corona poling setup was completely enclosed by an environmental chamber which controlled the poling temperature. For the case of hot poling, the corona charge was maintained as the temperature was cooled from poling temperature of 145°C to room temperature. Room temperature samples were kept under the field for the same duration of 2 h. The corona field was kept in constant voltage of 6 kV at room temperature (hot poling) (145°C) as listed in Table I. The corona poling setup was completely enclosed by an environmental chamber (dashed enclosure in Fig. 1) which controlled the poling temperature. For the case of hot poling (samples 1 and 4), the corona charge was maintained as the temperature was cooled from poling temperature of 145°C to room temperature (25°C). Room temperature samples were kept under the field for the same duration of 2 h. The corona field was kept in constant voltage of 6 kV at 25°C in ambient.

Table I. Experimental details of six samples.

<table>
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<tr>
<th>Sample</th>
<th>Annealing</th>
<th>Poling</th>
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<tr>
<td>1</td>
<td>Yes</td>
<td>+6 kV at 145°C in ambient</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>+6 kV at 25°C in ambient</td>
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<td>3</td>
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<td>No</td>
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<tr>
<td>4</td>
<td>No</td>
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<tr>
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<tr>
<td>6</td>
<td>No</td>
<td>No</td>
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Poly(vinylidene fluoride) (PVDF) and the copolymer family [e.g., P(VDF-TrFE), P(VDF-HFP), P(VDF-TrFE-CtFE), etc.] have been studied for ferroelectricity in memory applications, electrostriction, piezoelectricity, as well as electromechanical applications. To enhance the remnant polarization properties, different electrical poling methods have been used, e.g., thermoelectrets and corona poling (Ref. 8 and 9 and the references therein). The major advantage of corona poling over thermoelectrets is that electrodes are not required on the sample surface subjected to the corona field. This enables the possibility of a noninvasive modification of the film’s crystalline properties and also effectively reduces the likelihood of catastrophic local dielectric breakdown.

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Experimental

Thin film samples of copolymer P(VDF-TrFE) of 70–30 mol% were prepared by spincoating. A solution of copolymer powder was prepared with methyl ethyl ketone solvent at a concentration of 30 mg/mL and filtered through 0.45 μm pore size. Indium-doped tin oxide (ITO) coated glass substrate was cleaned with acetone, methanol, and deionized water. The copolymer solution was then spin coated on the glass substrates to yield 350 nm thick films as determined by Tencor Alpha-Step 500 surface profiler. Samples prepared with the same condition of spin coating were then subjected to different heating and poling conditions. Some of the samples were preannealed in nitrogen ambient at 142°C for 2 h to enhance the crystallinity. They were then poled at either room temperature (25°C) or elevated temperature (hot poled) (145°C) as listed in Table I. The corona poling setup was completely enclosed by an environmental chamber (dashed enclosure in Fig. 1) which controlled the poling temperature. For the case of hot poling (samples 1 and 4), the corona charge was maintained as the temperature was cooled from poling temperature of 145°C to room temperature (25°C). Room temperature samples were kept under the field for the same duration of 2 h. The corona field was kept in constant voltage of 6 kV at 25°C in ambient.

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mode and the current in the circuit was monitored. The metal-polymer-metal capacitor devices were fabricated by thermal evaporation of gold electrodes onto the P(VDF-TrFE) film using a shadow mask.

Surface morphology of samples was examined by atomic force microscopy (AFM) (Digital Instrument Dimension 3100). Film crystalline structure was characterized using an X-ray diffractometer (XRD) Bruker AXS D8 DISCOVER with a two-dimensional (2D) general area diffraction detector system and Cu Kα source. Absorption spectra were measured by Ocean Optics USB4000 spectrometer using reflectance mode in the wavelength range from 200 to 850 nm. Blank ITO glass was initially scanned at the glass surface to serve as reference. X-ray photoelectron spectra were recorded with nonmonochromatic resolution and at pass energy of 23.5 eV.

For samples without thermal treatment (5 and 6), low intensity arcs were observed from the patterns that show low crystallinity, probably of short-range order, in a predominantly amorphous matrix. A preferred crystalline orientation can also be seen from the annealed and hot-poled sample 1 with the appearance of a distinctively bright band at the center of the arc, whereas a uniform arc indicating a lack of texture is observed in the nonannealed but hot-poled sample 4. The brighter color of the arcs (as seen from the intensity chart) also suggests higher crystallinity in samples 1 and 4 as compared to samples 2 and 3. As evident from the 2D X-ray data (Fig. 2a), all the annealed samples (1–3) show good crystallinity, whereas the hot poling seems to induce high texture (sample 1) and improved crystallinity (sample 4).

From the integrated intensity data (shown in Fig. 2b), only one dominant crystalline peak was observed in all the samples. The strong peak in 2θ range of 19°–20° results from a doublet consisting of (110) and (200) diffraction that are contributed by both paraelectric, α, and ferroelectric, β, phases, respectively. The d spacing nearly constant for all samples at 4.47 ± 0.01 Å indicates the packing of polymer chains is not affected by the interaction of thermal treatment (annealing or heating during hot poling) and poling field. Lamellar crystal sizes, determined from the Scherrer equation, are in the range of 10–10.7 nm, in agreement with previously reported data.

The XRD intensity reveals that room-temperature poling does not have any effects on film crystallinity by comparing results between samples 2 and 3 as well as between samples 5 and 6. In both cases, it is probable that the restriction of polymer chains in the solid state was much stronger compared to the field strength. Prior to hot poling, sample 1 should have a semicrystalline structure similar to sample 3 due to preannealing, while sample 4 would mainly contain...
the amorphous phase like sample 6. From Fig. 2b and results from the above calculations, it is evident that after hot poling, samples 1 and 4 both possess similar crystalline characteristics.

AFM studies display a preferential orientation of grains for hot-poled sample 1 (Fig. 3a) while AFM image of room temperature-polled sample 2 (not presented here) shows similar characteristics as that of sample 3 (Fig. 3b), with randomly oriented grains. It is estimated that the orientation of the grains in sample 1 is nearly perpendicular to the direction of the poling electrode wire; hence folding polymer chains are nearly parallel to the poling wire. Similar orderly rearrangement of P(VDF-TrFE) rod-like crystals has been previously reported.16 Hence, hot-poling process can be similarly used to obtain ordered structure of semicrystalline ferroelectric thin films without invasive contact to the sample surface. Corona poling effects were also examined in amorphous films (samples 4 and 5). While sample 4 exhibits high crystallinity but randomly oriented grains with smaller size, sample 5 (not shown) had similar crystallinity and surface morphology as sample 6. The morphology of samples 2 and 5 could be anticipated since the required energy for the polymer chains in solid state to become mobile is much larger than that provided by the corona field alone at low temperatures.

A characteristic rod-like grain structure or edge-on crystal is observed in AFM images of the annealed sample 3 (Fig. 3b). Each rod-grain has a length of ~600 nm and consists of a multislab thickness of ~60 nm. This is about two times longer and slightly thicker compared with other reports,17,18 possibly due to the higher annealing temperatures used in this study that leads to the growth of larger grains. For the hot-poled sample 4 (Fig. 3c), smaller rod-like grains were observed with average sizes of 200 nm long and 50 nm thick. The formation of these small and random grains in sample 4 is attributed to thermal activation from the hot-poling process leading to crystalline structure as observed by XRD (Fig. 2a and b).

We attribute the difference of crystal sizes between samples 1, 3, and 4 to the interaction of different thermal conditions with the presence of the poling field. During annealing, polymer chains were disentangled from the amorphous regions and folded into crystalline lamellae through gliding motion. However, in the presence of corona charges created by the poling field, dipolar moments were anchored at the top surface thus hindering the motion and rearrangement of the chains. This opposite effect, therefore, limited the crystal sizes and prevented orientation of rod-like grains. For sample 1, crystalline grains had been formed during the annealing step (similar to sample 3) which led to a stronger response to the subsequently applied poling field at elevated temperature and resulted in formation of longer grains possibly by joining of grains.

To further confirm the organized structure in the hot poled samples, UV-vis absorption spectra were obtained (Fig. 4), with the strongest absorption occurring in the 350–400 nm range. The existence of the absorption peak in UV-vis spectra of P(VDF-TrFE) copolymer can be viewed under the effects of electron donation into antibonding orbitals of the C–F bond.19,20 Preannealed and hot-poled sample 1 and hot-poled sample 4 show the highest absorbance intensity and exhibit a shift of absorption peak to longer wavelengths (bathochromic). We attribute the increased absorption to the enhanced crystallinity due to heat-treatments. In the pre-annealed and hot-poled sample 1 and the hot-poled sample 4, more ferroelectric phase was formed after poling, hence more F pairs were aligned on the same side of the polymer chain. This would eventually lead to easier excitation and donation of electrons from np orbitals of F atoms to antibonding orbitals ω of C–F bond by the excitation light.

The bathochromic shift has been seen in polymer-dye films subjected to elevated temperature corona poling20 and is explained based on electrochromism in which large electrostatic charges induced by corona fields accumulate near the sample surface. For the reported polymer-dye system, the bathochromic shift was seen to disappear after ten days due to slow depletion of charges.21 The shifts in our experiment were found to be unchanged upon retesting after 60 days. This is attributable to the longer retention of injected charges by semicrystalline structures of the copolymer film that consists of crystalline phases embedded in an amorphous matrix. During the poling process, ferroelectric dipoles were aligned according to the field direction, which was accompanied by a simultaneous charge injecting into the film surface to compensate for the potential built up by the dipole moment. The injected charges could reside in the amorphous phase or at the crystalline-amorphous interface region for a long time due to stability of the polarization dipoles.

High frequency (1 MHz) capacitance measurement (C-V) was used to characterize the changes in dielectric properties of the poled film. Measurements performed on a metal-polymer-metal capacitor device (Fig. 5) display butterfly shaped hysteresis behavior, characteristic of ferroelectric materials, for samples subjected to annealing treatments (samples 1, 2, and 3); whereas, samples not subjected to annealing (samples 4, 5, and 6) failed to give stable data due to
high conductivity. We believe the high conductivity was caused by the porosity of the amorphous phase which led to diffusion of gold during thermal evaporation of the top electrode. Hot-poled and annealed samples showed the largest capacitance, the increment being attributed to ferroelectric phase formation in hot-poled samples, contributed by significant dipolar alignment and injected charges for compensation. As opposed to hot-poled sample 1, the capacitance values of room-temperature poled sample 2 showed a drastic reduction in capacitance (Fig. 5) after just one day of storage. This reduction in capacitance suggests that room-temperature corona poling had only led to charge accumulation on the sample surface, leading to a discharging effect upon the removal of the external field.

Characterizations by X-ray photoelectron spectroscopy (XPS) (Fig. 6) indicate four different C states exist in C 1s deconvoluted spectra, e.g., 282.22 eV organic contaminants, 284.82 eV saturated hydrocarbon CH2, 287.51 eV–CFH, and 289.79 eV–CF2. While the positions of CF2 and CF2 peak have been well determined, the CFH component was determined by comparison of its shift from CF2 and correlated to the characteristics of poly(trifluoroethylene) as reported in Ref. 22. Spectra of F 1s also clearly revealed two states of F atoms in the copolymer, namely 684.75 eV–CFH and 687.06 eV– CF2, due to differences in the bonding environment. Scans in O 1s region showed similar spectra for all six samples and was attributed to the presence of organic traces in the analysis chamber. Summary of peak positions of C 1s and F 1s is shown in Table II after charge compensation using the equipment reference C 1s peak.

A clear trend of peak shifting in the spectra of both C and F atoms is evident in Fig. 6 and Table II. Samples 1 and 4 show similar C 1s and F 1s binding energies, which indicate the similar atomic binding states, hence a similar process of chain folding and reorientation during poling at elevated temperature. After hot poling, the environment of the atoms shows to be unaffected by preexisting crystalline/amorphous structure or joining of rod-like grains. Room-temperature poling is seen to have more pronounced effects to the pre-annealed samples compared to the nonannealed one, comparing samples 2 and 5. We suggest this is related to the formation of a new polarizable phase (αp) in the semicrystalline sample. It has been reported that electret poling of crystalline PVDF film under similar conditions (field of 1500 kV/cm at 24°C for 3 h) led to new formation of αp phase without any changes to the α and β phase observed at (110, 200) diffraction.23 This observation also explains the identical XRD data obtained for samples 2 and 3.

Figure 7 shows the compositions of C 1s components and the ratio of hydrocarbon CH2 to fluorine-bonding carbons (CF2 + CFH) in all six samples. The data show clear differences in the effect of poling samples of semicrystalline and amorphous structure. Annealed samples displayed an overall increment of fluorine-bonded carbons bonding against hydrocarbon bonds. Hot-poled sample 1 is seen to have the highest percentage of (CF2 + CFH) component suggesting that the applied positive corona poling function.

Table II. Summary of binding energy (eV) values for components of C 1s and F 1s.

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<th>Sample</th>
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<th>3</th>
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<td>684.97</td>
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![Figure 5](image1.png) **Figure 5.** (Color online) High frequency capacitance-voltage measurement of the metal-polymer-metal devices.

![Figure 6](image2.png) **Figure 6.** XPS spectra for C 1s and F 1s core orbitals. Deconvolution and curve-fitting were done using 70% Gaussian–30% Lorentzian shape function. Highlighted area shows deconvoluted curves for C 1s and F 1s spectra.
induced the relocation of more fluorine atoms containing higher electron density towards the top surface of the copolymer film sample. This indicates a change in chemistry of the top surface of the films, the compatibility of which with subsequent multilayers may need to be considered to ensure optimal device integrity and functionality.

Conclusion

We have characterized and correlated the changes in structure to the dielectric properties of spin-coated ferroelectric P(VDF-TrFE) (70–30 mol %) thin films after subjecting to corona poling. Thermal treatment by annealing or hot-poling affects rod-like grain structure on the film surface resulting in different sizes and arrangement. Poling at elevated or room temperature strongly enhances crystallinity, grain formation and orientation, the resultant capacitance values, as well as changes in bonding energies of the region near the top surface. The increased crystallinity by hot poling is independent of pre-poling crystallinity; however, grain size analysis suggests the absence of recrystallization. Chemistry at regions near poled surface is altered with more appearance of fluorine and shifts of core orbital to higher binding energies. The increased amount of electronegative F atoms agrees with the strong response of ferroelectric dipoles to the positive corona poling. As a result, the improvement of dielectric properties with higher capacitance values and longer retention can be well correlated to the enhanced crystallinity and increased ferroelectric phase after hot poling. It can be seen that corona poling is a feasible and advantageous method in creating ordered structure and improving ferroelectric-dielectric properties with its noninvasive nature.

Acknowledgments

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References