<table>
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<th>Title</th>
<th>Enhanced functional and structural characteristics of poly(vinylidene-trifluoroethylene) copolymer thin films by corona poling</th>
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<td>Author(s)</td>
<td>Nguyen, Chien A.; Lee, Pooi See; Yee, Wu Aik; Lu, Xuehong; Srinivasan, Madhavi; Mhaisalkar, Subodh G.</td>
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Poly(vinylidene fluoride) (PVDF)\textsuperscript{1,2} and the copolymer family [e.g., P(VDF-TrFE), P(VDF-HFP), P(VDF-TrFE-CTrFE), etc.] have been studied for ferroelectricity in memory applications, electrostriction, piezoelectricity, as well as electromechanical applications.\textsuperscript{4,5} To enhance the remnant polarization properties, different electrical poling methods have been used, e.g., thermoelectrets\textsuperscript{6} 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 nonintrusive 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 ($>10 \mu m$ thickness) films.\textsuperscript{8,9} 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 $\mu m$ 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 temperatures below the melting point.\textsuperscript{2} 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 thermal treatment, it is expected to have great effects on the formation of crystalline phases and grains even in the solid state of the copolymer film. This eventually leads to changes in topographic characteristics, dielectric and optical properties of the poled films. Understanding these changes will help gain further insights into the dielectric material science and technology of ferroelectric thin film.

While thick ferroelectric polymer films are usually used as a stand-alone part in many applications, thin films are an essential functional layer in multilayered devices. Characteristics of poled films supported by a substrate are hence of great interest as structural changes by poling are constrained by the film-substrate adhesion. Furthermore, in multilayered functional films, surface morphology of poled films is also important in understanding the interfacial formation and functional interactions within the multilayered structure. One such example is the application of P(VDF-TrFE) thin films in organic nonvolatile memory devices in which the ferroelectric copolymer layer is deposited on a substrate surface and forms direct interfacial contact with an organic semiconducting film.\textsuperscript{5} Such devices hold a great promise for realizing low-cost nonvolatile memory devices that could be either used in all plastic electronics applications\textsuperscript{7} or could potentially be integrated with Si devices.\textsuperscript{10}

In this article, we investigate the effects of corona poling on P(VDF-TrFE) thin films by examining the changes in surface morphology, crystalline structure, chemical composition, dielectric and optical properties. We also examine the role of annealing and high-temperature poling in the alignment of crystalline grains with a preferential orientation in the ferroelectric polymer film.

### 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 $\mu m$ 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.\textsuperscript{11} 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.

<table>
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<tr>
<th>Sample</th>
<th>Annealing</th>
<th>Poling</th>
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<tbody>
<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>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>No</td>
<td>+6 kV at 145°C in ambient</td>
</tr>
<tr>
<td>5</td>
<td>No</td>
<td>+6 kV at 25°C in ambient</td>
</tr>
<tr>
<td>6</td>
<td>No</td>
<td>No</td>
</tr>
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</table>

\textsuperscript{4} E-mail: acnguyen@nanyu.edu.sg; psee@ntu.edu.sg
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 using nonmonochromatic resolution and at pass energy of 23.5 eV.

Temperature was provided by the environment chamber (Color online). The heating state was much stronger compared to the field strength. Prior to hot poling, sample 1 should have a semicrystalline structure similar to the 2D X-ray data 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 an effect 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 a preferred crystalline orientation, as seen from the intensity chart of the copolymer film. 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.

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Results and Discussion

Figures 2a and b show the x-ray diffraction patterns and the integrated intensity from the patterns of all six samples. As the 2D detector was used, diffraction data are no longer limited to measurement only in the diffractometer plane. Instead, a larger portion of the diffraction rings can be recorded, which is preferred in this study because it could provide more information on the crystal orientation related to the forming of crystalline grains. From Fig. 2a, thermal-treated samples (1, 2, 3, and 4) show typical crystalline structure with the appearance of bright arc patterns. The arcs, which were formed by the intersection of the diffracting cones and the 2D detector moving in the diffractometer plane, indicate polycrystalline structure of the copolymer film. 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).

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Figure 1. (Color online) Diagram of corona field poling setup. The heating temperature was provided by the environment chamber (dashed enclosure box).

Figure 2. (Color online) Two-dimensional X-ray diffraction characterization of all six samples (a) diffracting patterns and (b) integrated data from the patterns.
we also examined in amorphous films

corona charges created by the poling field, dipolar moments were an-

chored at the top surface thus hindering the motion and rearrange-

ment 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 subse-

quently 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 \( \sigma^* \) orbitals of the C–F bond. 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 \( n_p \) orbitals of F atoms
to antibonding orbitals \( \sigma^* \) of C–F bond by the excitation light.

The bathochromic shift has been seen in polymer-dye films
subjected to elevated temperature corona poling and is explained
based on electrochromism in which large electrostatic charges in-
duced 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.

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 simul-
taneous 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, charac-
teristic 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

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**Figure 3.** (Color online) AFM images of (a) sample 1, (b) sample 3, (c) sample 4, and (d) sample 6. All scan dimensions are 5 \( \mu \)m \( \times \) 5 \( \mu \)m.

**Figure 4.** (Color online) UV-vis absorption spectra in 300–700 nm range for samples 1, 3, 4 and 6. The strongest absorption is seen to be in range 350–400 nm wavelength.
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 CH2 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.

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

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<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
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<td>687.37</td>
<td>686.62</td>
<td>687.36</td>
<td>686.57</td>
<td>686.95</td>
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<tr>
<td>CFH</td>
<td>685.07</td>
<td>684.97</td>
<td>684.44</td>
<td>684.76</td>
<td>684.35</td>
<td>684.64</td>
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</table>

Figure 5. (Color online) High frequency capacitance-voltage measurement of the metal-polymer-metal devices.

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.

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