Enhanced functional and structural characteristics of poly(vinylidene-trifluoroethylene) copolymer thin films by corona poling

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

2007

Nguyen, C. A., Lee, P. S., Yee, W. A., Lu, X., Srinivasan, M., & Mhaisalkar, S. G. (2007). Enhanced functional and structural characteristics of poly(vinylidene-trifluoroethylene) copolymer thin films by corona poling. *Journal of the electrochemical society*, 154(10), G224-G228.

<https://hdl.handle.net/10356/95676>

<https://doi.org/10.1149/1.2769269>

© 2007 The Electrochemical Society. This paper was published in *Journal of The Electrochemical Society* and is made available as an electronic reprint (preprint) with permission of The Electrochemical Society. The paper can be found at the following DOI: [<http://dx.doi.org/10.1149/1.2769269>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

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

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

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

Electrical poling is of much interest for the enhancement of polarization properties of ferroelectric materials such as poly(vinylidene-trifluoroethylene) [P(VDF-TrFE)] in applications ranging from memory devices to piezoelectric actuation. Here, we report the changes in dielectric and optical properties correlated with structural modification of P(VDF-TrFE) thin films (<1 μm thickness) subjected to corona poling at low voltages (6 kV) under various thermal conditions. Enhanced crystallinity of hot-poled samples was observed independent of thermal history and crystalline structure, indicating the absence of recrystallization during poling. Absorption measurements confirmed the ordered structure in hot-poled samples due to the permanent orientation of the dipoles and higher crystallinity, thus resulting in increased and long-retained capacitance of the ferroelectric P(VDF-TrFE) capacitor device from high frequency *C-V* characterization. X-ray photoelectron spectroscopy further confirmed the shifting of C and F core orbitals to higher binding energy is related to formation of more ferroelectric phases by corona poling. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2769269] All rights reserved.

Manuscript submitted January 19, 2007; revised manuscript received June 11, 2007. Available electronically August 16, 2007.

Poly(vinylidene fluoride) (PVDF)^{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,³ electrostriction, piezoelectricity, as well as electromechanical applications.^{4,5} To enhance the remnant polarization properties, different electrical poling methods have been used, e.g., thermoelectrets^{6,7} 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 μm thickness) films.^{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 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.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 ferro-

electric copolymer layer is deposited on a substrate surface and forms direct interfacial contact with an organic semiconducting film.³ Such devices hold a great promise for realizing low-cost non-volatile memory devices that could be either used in all plastic electronics applications³ or could potentially be integrated with Si devices.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 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.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 I. Experimental details of six samples.

Sample	Annealing	Poling
1	Yes	+6 kV at 145°C in ambient
2	Yes	+6 kV at 25°C in ambient
3	Yes	No
4	No	+6 kV at 145°C in ambient
5	No	+6 kV at 25°C in ambient
6	No	No

^z E-mail: acnguyen@pmail.ntu.edu.sg; pslee@ntu.edu.sg

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

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 K α 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 PHI 5600 spectrometer using Mg K α (1253.6 eV) source at a base pressure of 3.5×10^{-9} Torr. The measurement was performed with nonmonochromatic resolution and at pass energy of 23.5 eV. High frequency capacitance-voltage data were obtained from a HP4284 LCR meter, operating at 1 MHz, 15 mV amplitude, and forward/reversed voltage sweeping.

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.¹² 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.¹³ The d spacing nearly constant for all samples at 4.47 ± 0.01 Å indicates the pack-

(a)

(b)

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

ing 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,¹⁴ are in the range of 10–10.7 nm, in agreement with previously reported data.¹⁵

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

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

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-poled 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 $\sim 600\ \text{nm}$ and consists of a multislabs thickness of $\sim 60\ \text{nm}$. 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 $200\ \text{nm}$ long and $50\ \text{nm}$ 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 an-

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.

chored 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 σ^* 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 n_p orbitals of F atoms to antibonding orbitals σ^* of C–F bond by the excitation light.

The bathochromic shift has been seen in polymer-dye films subjected to elevated temperature corona poling²¹ 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

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

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 CH_2 , 287.51 eV- CFH , and 289.79 eV- CF_2 . While the positions of CH_2 and CF_2 peak have been well determined, the CFH component was determined by comparison of its shift from CF_2 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- CF_2 , 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 (α_p) 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 forma-

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.

tion of α_p 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 CH_2 to fluorine-bonding carbons (CF_2 + 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 (CF_2 + CFH) component suggesting that the applied positive corona poling

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

Sample	1	2	3	4	5	6
CF_2	290.35	290.47	289.61	290.31	289.31	289.68
CFH	288.25	288.33	287.60	288.26	287.36	287.40
CF_2	687.31	687.37	686.62	687.36	686.57	686.95
CFH	685.07	684.97	684.44	684.76	684.35	684.64

Figure 7. Relative area percentages of hydrocarbon CH_2 and fluorine-bonding carbon ($\text{CF}_2 + \text{CFH}$) (left axis) and the ratio of them (right axis).

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

We are very grateful to M. Z. Tun for obtaining the XPS data. One of the authors, C.A.N., would like to acknowledge the research scholarship awarded by Nanyang Technological University. This work is supported by A*Star grant no. 0521170032 and NTU RG26/05 grant no. M52070034.

Nanyang Technological University assisted in meeting the publication costs of this article.

References

1. A. J. Lovinger, *Science*, **220**, 1115 (1983).
2. T. Furukawa, *Adv. Colloid Interface Sci.*, **71-72**, 183 (1997).
3. R. C. G. Naber, C. Tanase, P. W. M. Blom, G. H. Gelinck, A. W. Marsman, F. J. Touwslager, S. Setayesh, and D. M. De Leeuw, *Nat. Mater.*, **4**, 243 (2005).
4. Q. M. Zhang, V. Bharti, and X. Zhao, *Science*, **280**, 2101 (1998).
5. S. B. Lang and S. Muensit, *Appl. Phys. A: Mater. Sci. Process.*, **85**, 125 (2006).
6. H. Sussner and K. Dransfeld, *J. Polym. Sci., Part A-2*, **16**, 529 (1978).
7. M. A. Marcus, *J. Appl. Phys.*, **52**, 6273 (1981).
8. J. A. Giacometti and A. S. DeReggi, *J. Appl. Phys.*, **74**, 3357 (1993).
9. S. N. Fedosov, A. E. Sergeeva, G. Eberle, and W. Eisenmenger, *J. Phys. D*, **29**, 3122 (1996).
10. N. Yamauchi, *Jpn. J. Appl. Phys., Part 1*, **25**, 590 (1986).
11. T. Furukawa, H. Matsuzaki, M. Shiina, and Y. Tajitsu, *Jpn. J. Appl. Phys., Part 2*, **24**, Part 2 L661 (1985).
12. B. B. He, J. Anzelmo, P. LaPuma, U. Preckwinkel, and K. Smith, *Adv. X-Ray Anal.*, **44**, 1 (2001).
13. A. J. Lovinger, G. T. Davis, T. Furukawa, and M. G. Broadhurst, *Macromolecules*, **15**, 323 (1982).
14. B. D. Cullity, *Elements of X-Ray Diffraction*, p. 102, Addison-Wesley, New York (1977).
15. K. Matsushige and H. Yamada, *Ann. N.Y. Acad. Sci.*, **960**, 1 (2002).
16. K. Kimura, K. Kobayashi, H. Yamada, T. Horiuchi, K. Ishida, and K. Matsushige, *Eur. Polym. J.*, **40**, 933 (2004).
17. Y. J. Park, S. J. Kang, C. Park, K. J. Kim, H. S. Lee, M. S. Lee, U. Chung, and I. J. Park, *Appl. Phys. Lett.*, **88**, 242908 (2006).
18. X. Chen, H. Yamada, T. Horiuchi, and K. Matchushige, *Jpn. J. Appl. Phys., Part 2*, **37**, 3834 (1998).
19. W. T. Borden, *Chem. Commun. (Cambridge)*, **1998**, 1919.
20. E. Gianetti, *Polym. Int.*, **50**, 10 (2001).
21. M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, and A. Dienes, *J. Opt. Soc. Am. B*, **6**, 733 (1989).
22. D. T. Clark, W. J. Feast, D. Kilcast, and W. K. R. Musgrave, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 389 (1973).
23. D. Naegel, D. Y. Yoon, and M. G. Broadhurst, *Macromolecules*, **11**, 1297 (1978).