High Polarization Levels in Poly(vinylidene fluoride–trifluoroethylene) Ferroelectric Thin Films Doped with Diethyl Phthalate

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ABSTRACT: With a spin-coating technique, ferroelectric thin films of poly(vinylidene fluoride–trifluoroethylene) copolymer [P(VDF–TrFE; with a content (mol %) ratio of 68/32 vinylidene fluoride/trifluoroethylene] were fabricated on silicon wafers covered with platinum and were doped with a nucleation agent, diethyl phthalate (DEP). The remnant polarization of copolymer thin films increased 70% after doping with DEP, and the coercive field was reduced, which is highly desirable in bistable memory devices. The dielectric constant of thin films also increased after doping. However, the effect of doping on the ferroelectric response was not remarkable in freestanding copolymer films. The results demonstrated that the ferroelectric dipole orientation in P(VDF–TrFE) thin films was significantly enhanced by the presence of DEP because the crystallinity of thin films decreased after doping, as revealed by X-ray results. The dopant DEP acted as both a nucleation agent during the crystallization process and a plasticizer in the noncrystalline regions, which greatly enhanced the dipole orientation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1416–1419, 2003

INTRODUCTION

Ferroelectric polymer thin films have attracted a great deal of attention in recent years because of their emerging applications in electronics, photonics, microsensors, and actuators.[1–3] The investigation of ultrathin ferroelectric polymer films will be helpful to the understanding of the fundamental question of the critical size of the film or domain. Moreover, numerous applications of ferroelectric polymer ultrathin films are predicted to emerge. For example, they can be used as interlayer dielectrics with less crosstalk in microelectronics devices and as ferroelectric memory elements in computers and intelligent cards. The use of ferroelectric polymers in thin film forms can produce fully integrated devices in which polarization switching can occur in low voltages and can reduce the size and weight of devices. Because of the extremely high coercive electric field (E_c) of ferroelectric polymers, it is particularly necessary to fabricate these copolymers into ultrathin films. However, the results of our recent research and also other groups' research in the thickness dependence of the polarization behavior of poly(vinylidene fluoride–trifluoroethylene) copolymer [P(VDF–TrFE)], which is the most widely used ferroelectric polymer, films showed that the polarization level decreased and the switching field increased as the thickness was reduced, and a large drop in the polarization level was observed as the thickness was reduced to below 100 nm.[4–9] Hence, how to increase the polarization level and reduce the switching field become crucial for the practical application of ferroelectric thin and ultrathin films and also remains a challenge.

In P(VDF–TrFE) polymer films, polarization behavior is directly related to crystallinity, crystal orientation, and crystallite size in the film. As the polymer film thickness reduced, it is expected that the surface and interface will play a significant role in the development of morphology and chain conformation of the films.[10,11] It is believed that in thin films, crystallization will be hindered because of the heterogeneous nucleation process from substrates, which determines the crystal orientation, and therefore, the nucleation agent will be helpful for the crystallization process. In this article, we report the ferroelectric behavior of P(VDF–TrFE) thin polymer films doped with diethyl phthalate (DEP), which is commonly used as a nucleation agent in polymer engineering. We show that the remnant polarization (P_r) of the thin films doped with DEP increased remarkably. In addition, the dielectric constant of thin films also increased after doping.

EXPERIMENTAL

Sample preparation

P(VDF–TrFE) copolymer with a content (mol %) ratio of 68/32 vinylidene fluoride/trifluoroethylene was chosen for this study because copolymer with this composition is in the ferroelectric phase at room tem-
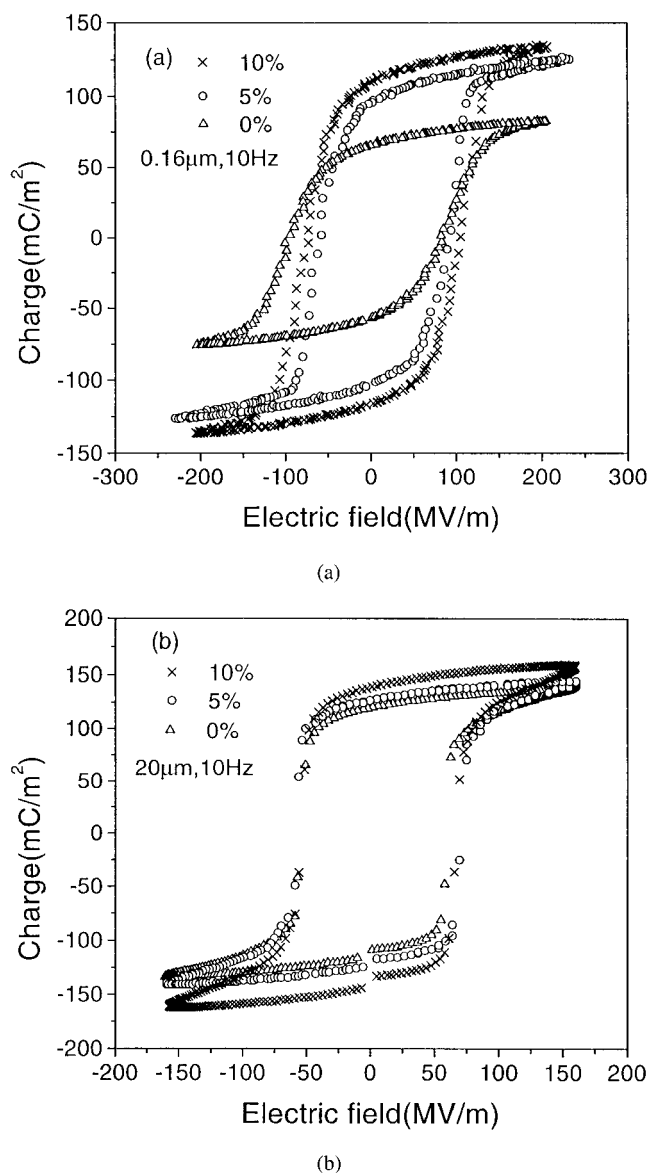
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(a)

(b)

Figure 1 Polarization hysteresis loops for (a) P(VDF–TrFE) 68/32 and (b) freestanding P(VDF–TrFE) 68/32 copolymer thin films with 0, 5, and 10% DEP.

perature when prepared by solution casting. The weight-average molecular weight is about 200,000. The thin films of this copolymer were deposited on silicon wafers covered with platinum (NOVA Electronic Materials Inc., Mahwah, NJ) by the spin-coating technique from a dimethylformamide (DMF) solution. For doped films, DEP was added into the solution during the solvation of the copolymer powder. The solution was filtered with a 0.2-μm filter before spin coating. The thickness of the film (70 nm to 1 μm) was controlled by both the rate of revolution of the spinner and the concentration of the solution. The thickness was determined by an Alpha-step 500 surface profiler (Tencor Instruments, Mountain View, CA). The films were annealed in a vacuum oven at 140°C for 2 h and

then cooled down slowly to room temperature. Aluminum was evaporated on the thin film surface to form the top electrode (the diameter was around 2 mm and was calibrated by optical microscopy), and the platinum on Si was used as the bottom electrode. For comparison, freestanding copolymer films with and without DEP were also detected. The freestanding films were prepared by solution casting from DMF solution and were then stretched up to five times of their initial length. The stretched films were annealed in a vacuum oven at 140°C for 6 h. The samples used for polarization measurement were sputtered with gold electrodes on both surfaces.
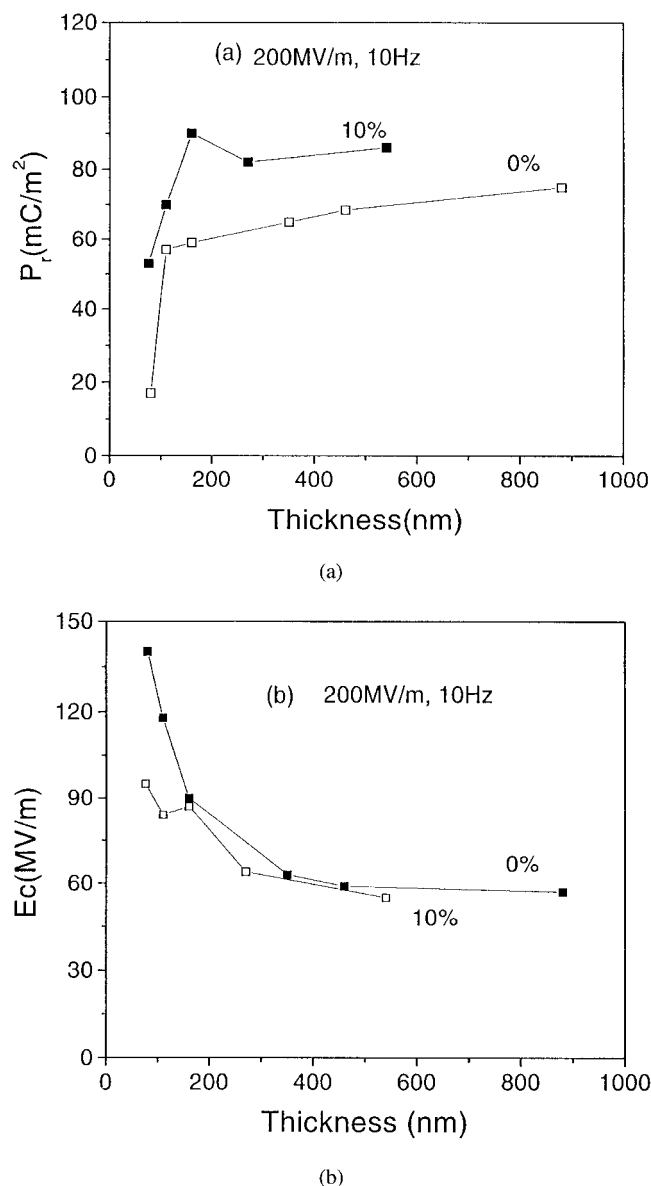

(a)

(b)

Figure 2 Variation of polarization parameters of P(VDF–TrFE) copolymer films with different thickness under 200 MV/m and 10 Hz: (a) P_r and (b) E_c.

Measurements

The polarization hysteresis loops were recorded with the Sawyer–Tower technique. An external electric field was applied in the form of a triangular wave with a frequency of 10 Hz at different amplitudes. The dielectric constant (ϵ') of the film was calculated from the capacitance by the formula of a parallel plate capacitor

$$\varepsilon' = \frac{Ct}{\varepsilon_0 A} \qquad (1)$$

where C is the capacitance of the metal–insulator–metal element, which was recorded on an HP 4192A impedance analyzer; A is the area of the top electrode, which was measured by optical microscopy with a scaled-eye lens; and ϵ_0 (= 8.85×10^{-12} F/cm) is the permittivity of free space. The X-ray patterns were taken at room temperature with a Scintag (Sunnyvale, CA) diffractometer with filtered Cu Kα radiation.

RESULTS AND DISCUSSION

For thin film device applications utilizing P(VDF–TrFE) copolymer, ferroelectric response in the films is of prime importance. The polarization hysteresis loops were measured at room temperature on the both doped and undoped P(VDF–TrFE) 68/32 thin films of different thickness. Presented in Figure 1(a) is the typical hysteresis loops of the thin films with 0, 5, and 10% DEP. The thickness of the films was 0.16 μm. As is shown in the figure, after doping with DEP, P_r of the thin films increased significantly. For example, for 0.16-μm films doped with 10% DEP, P_r under 200 MV/m at 10 Hz increased 70%. The E_c was as low as that of the undoped films or was even reduced after doping. High P_r and low E_c values are needed for bistable memory devices.

For comparison, the ferroelectric responses of freestanding P(VDF–TrFE) copolymer films were also measured. Figure 1(b) shows the hysteresis loops measured on 20 μm films with 0, 5, and 10% DEP. The polarization level of films also increased after doping with DEP, but the increase was not as much as that in thin films. It is well known that DEP is a commonly used nucleation agent for polymer crystallization.[12] In polymer thin films, the stiff substrate may hinder crystallization. The addition of DEP is helpful to the crystallization process. However, for freestanding P(VDF–TrFE) thick films prepared by solution casting, the crystallinity was high, and the P_r also increased proportionally after annealing.[5] Therefore, for annealed bulk copolymer films, the effect of nucleation agent was not as notable as that observed in thin films.

P_r and E_c of P(VDF–TrFE) 68/32 copolymer thin films were measured as a function of film thickness because P_r and E_c are the most direct indicators of
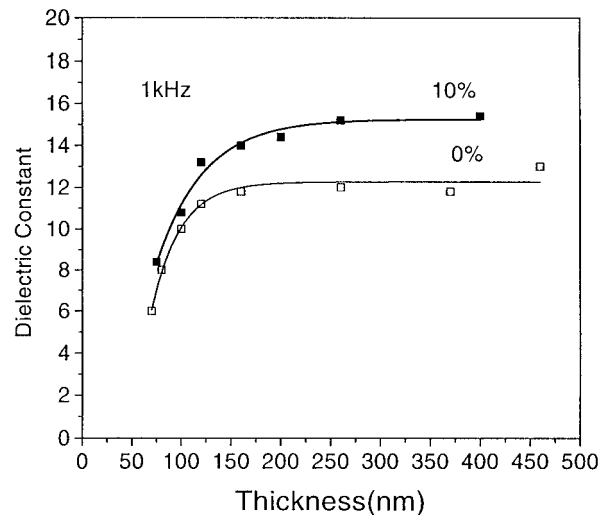

Figure 3 Thickness dependence of the dielectric constant of P(VDF–TrFE) thin films with 0 and 10% DEP.

ferroelectric properties. For films thicker than 0.1 μm, square and symmetric loops were observed. However, as the thickness was reduced to below 0.1 μm, the hysteresis loops became glossy and asymmetric. Figure 2 shows the variations of P_r and E_c with the film thicknesses for thin films with 10% DEP obtained from the polarization loops under 200 MV/m maximum applied field at 10 Hz, which were compared with undoped copolymer films with the same thicknesses. P_r of P(VDF–TrFE) films doped with 10% DEP was much higher and E_c was lower than those of undoped films. A high P_r and low E_c is highly desirable for bistable memory devices. These features indicate that the use of DEP dopant improved the polarization properties of the ferroelectric thin films.

Dielectric properties were also measured on doped P(VDF–TrFE) copolymer thin films with different thicknesses. Figure 3 shows the variation of the real part of the dielectric constant at 100 Hz with thickness for doped thin films with 10% DEP, and the results for the undoped copolymer thin films is also shown for comparison. For both doped and undoped films, the dielectric constant gradually decreased as the thickness changed from 0.4 to 0.1 μm. There was an abrupt drop in the dielectric constant when the thickness was reduced to below 0.1 μm. The doped thin films had higher dielectric constants than the undoped thin films. The large drop in the measured dielectric constant with reduced thickness may have come from the decrease in the crystallinity of thin films and the interface effect, as we have discussed in previous articles.[7–9]

P(VDF–TrFE) copolymer is a semicrystalline polymer in which small crystallites are surrounded by amorphous regions. It is well known that the ferroelectric response and dielectric properties are mainly from the crystalline phase. It was expected that the
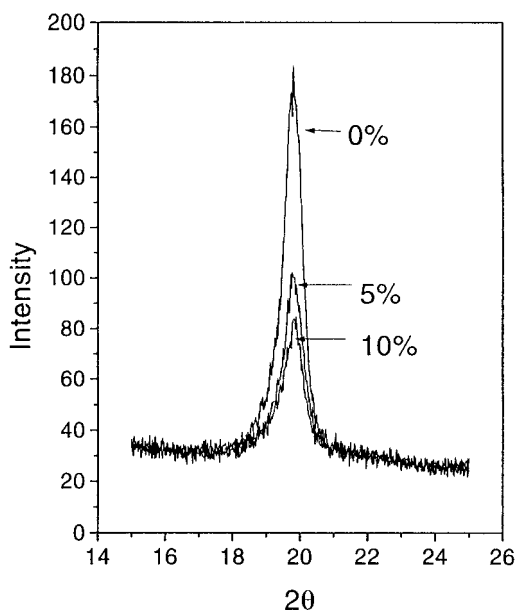
Figure 4 X-ray diffraction of P(VDF–TrFE) 68/32 copolymer films with 0, 5, and 10% DEP.

higher polarization level of P(VDF–TrFE) thin films was generated from higher crystallinity or crystal orientation. However, the X-ray results in Figure 4 showed that the crystallinity decreased after doping. In copolymer freestanding films, Omote et al. showed that the dielectric constant of the crystal strongly depends on the crystal orientation.[13] Therefore, we believe that the ferroelectric dipole orientation in P(VDF–TrFE) copolymer thin films was also significantly enhanced by the presence of DEP.

CONCLUSIONS

The doping effect on the dielectric and ferroelectric properties of P(VDF–TrFE) 68/32 copolymer films, fabricated on silicon wafers covered with platinum by the spin-coating technique, was studied. The polarization level of P(VDF–TrFE) thin films was significantly increased, and the coercive field was reduced after doping with DEP, which is highly desirable for bistable memory devices. The dielectric constant of thin films also increased after doping. All these results showed that in P(VDF–TrFE) copolymer thin films, the dopant DEP acted as both a nucleation agent during the crystallization process and a plasticizer in the non-crystalline regions, which greatly enhanced the dipole orientation.

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