

Dielectric Properties and Ferroelectric Behavior of Poly(vinylidene fluoride-trifluoroethylene) 50/50 Copolymer Ultrathin Films

HAISHENG XU*

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: Ultrathin films of poly(vinylidene fluoride-trifluoroethylene) copolymer [P(VDF-TrFE), with a content (mol %) ratio of 50/50 VDF/TrFE] were fabricated on silicon wafers covered with platinum by a spin-coating technique, ranging in thickness from 20 nm to 1 μm . The effect of thickness on dielectric properties and polarization behavior was investigated. A critical thickness was found to be about 0.1 μm . An abrupt drop of dielectric constant was observed, although there is no significant change in dielectric loss at this thickness. Square and symmetric hysteresis loops were obtained in films thicker than 0.1 μm . However, for films thinner than 0.1 μm , fewer square hysteresis loops were observed. SEM and X-ray results demonstrate that the effect of thickness on dielectric and ferroelectric properties could be explained by the changes of crystal structure in these films. In addition, the effects of irradiation on dielectric property and polarization response for ultrathin P(VDF-TrFE) films were also presented. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2259–2266, 2001

Key words: poly(vinylidene fluoride-trifluoroethylene) copolymer; ultrathin film; dielectric property; ferroelectricity

INTRODUCTION

The copolymers of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] have been studied extensively from the viewpoint not only of their ferroelectricity, piezoelectricity, and pyroelectricity but also of their applications in transducers, actuators, and sensors.^{1–4} The structural features of these copolymers with different TrFE composition have also been investigated in detail by means of FTIR spectroscopy, X-rays, and so forth.¹ However, most of these studies focused on the free-standing films thicker than 10 μm .

In recent years, the ferroelectricity of ultrathin P(VDF-TrFE) films, thinner than 1 μm , including Langmuir–Blodgett films, has attracted a great deal of attention.^{5–12} The investigation of ultrathin ferroelectric polymer films will be helpful to understand the fundamental question of the critical size of the film or grain. Moreover, numerous applications of ferroelectric polymer thin films are predicted to emerge. For example, they can be used as interlayer dielectrics with less cross talk in microelectronics devices and ferroelectric memory elements of a computer. Moreover, the use of ferroelectrics in thin form not only has a general advantage in reduced size and weight, but also has the ability of thin films to produce fully integrated devices in which switching can occur at low voltage. Because of the extremely high coer-

*E-mail: hxx3@psu.edu

cive electric field of P(VDF-TrFE) copolymers, it is particularly necessary to fabricate these copolymers into ultrathin films.

The methods to prepare ultrathin films include procedures such as spin coating, Langmuir-Blodgett (LB), and vacuum-deposition. The spin-coating process is relatively simple and the films have both high quality and wide thickness, ranging from tens of angstroms to several micrometers. It is the most common method in industry. In this study, the dielectric and ferroelectric properties of P(VDF-TrFE) 50/50 copolymer ultrathin films, which were prepared by the spin-coating technique, have been investigated. SEM and X-ray measurements were carried out to understand the relationship between properties and structure. After irradiation with high-energy electrons, significant changes of dielectric properties as well as polarization behavior were observed in the ultrathin films.

EXPERIMENTAL

Sample

For the present study, the random P(VDF-TrFE) copolymer powder with a content (mol %) ratio of 50/50 VDF/TrFE was supplied by Solvay and Cie (Brussels, Belgium), and the weight-average molecular weight was about 200,000. The ultrathin films of this copolymer were deposited on a silicon wafer covered with platinum (Nova Electronic Materials, Mahwah, NJ) by the spin-coating technique from a dimethyl formamide (DMF) solution. The solution was filtered in advance using a 0.2- μm filter. The thickness of the film (20 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 145°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 (2 mm in diameter), and the platinum on Si was used as the bottom electrode. For the irradiated ultrathin film, the irradiation was carried out in a nitrogen atmosphere with 2.55 MeV electrons at 95°C with the dosage of 50 Mrad.

Measurement

The capacitance and loss were recorded on an HP 4192A Impedance Analyzer. The dielectric con-

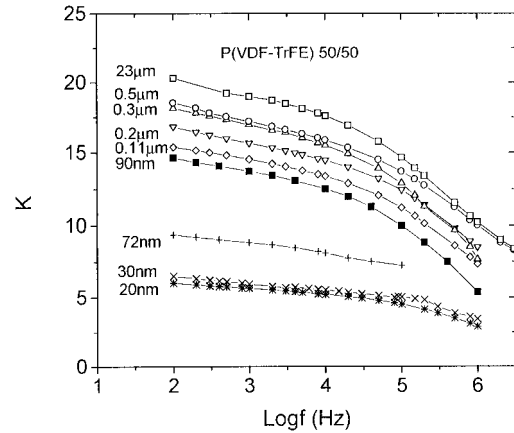


Figure 1 The frequency dependence of the dielectric properties of P(VDF-TrFE) 50/50 copolymer ultrathin films of varying thicknesses.

stant ϵ' of the film was calculated by the formula of a parallel plate capacitor

$$\epsilon' = \frac{Ct}{\epsilon_0 A} \quad (1)$$

where C is the capacitance of the metal-insulator-metal element; A is the area of the top electrode, which is measured by optical microscopy with a scaled-eye lens; and ϵ_0 ($=8.854 \times 10^{-12}$ F/m) is the permittivity of free space. The frequency dependence of the dielectric properties was measured with a range from 100 Hz to 1 MHz. The polarization hysteresis loops were recorded using the Sawyer-tower technique. An external electric field was applied in the form of triangular wave with a frequency of either 10 or 1 Hz, at different amplitudes. The X-ray patterns were taken at room temperature using a Scintag (Sunnyvale, CA) diffractometer with filtered Cu-K_α radiation. The surface of the film of different thicknesses was observed by scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Dielectric Properties

The dielectric properties were measured on ultrathin film samples of varying thicknesses. Figure 1 shows the frequency dependence of the real part of the dielectric constant, which decreases with the film thickness. The variation of K at 100 Hz

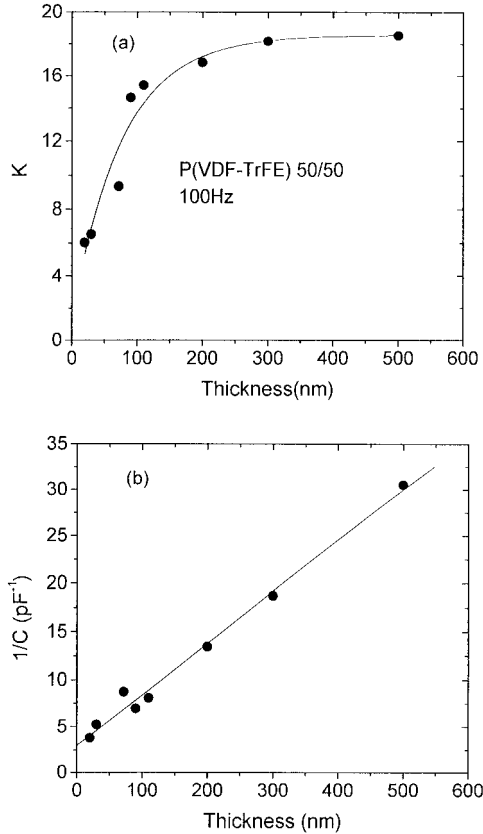


Figure 2 (a) The thickness dependence of the dielectric constant at 100 Hz replotted from Figure 1. (b) The reciprocal of unit area capacitance of thin films as a function of the film thickness for P(VDF-TrFE) 50/50 copolymer.

with thickness is summarized in Figure 2(a). The dielectric constant changes from 18 for thick films to about 6 for a 20-nm film. The dielectric constant gradually decreases as the thickness changes from 0.3 to 0.1 μm . There is an abrupt drop of the dielectric constant when the thickness is reduced to less than 100 nm. Meanwhile, there is no significant difference for dielectric loss in this thickness range. The loss is about 0.015 at low frequency and is about 0.3 at 1 MHz. There could be several reasons for the abrupt drop of the measured dielectric constant with reduced film thickness. One reason is the decrease of the crystallinity of P(VDF-TrFE) as the film thickness is reduced. It is generally believed that the dielectric and ferroelectric properties mainly come from the crystal phase. Recent studies on ultrathin polystyrene-derived film showed that the degree of crystallinity depends strongly on the film thickness.^{13,14} For the P(VDF-TrFE) 50/50 copoly-

mer studied here, the critical thickness is about 0.1 μm . The SEM and X-ray results support this explanation (see below).

Another possible reason is the existence of an effective interface region, which has lower effective dielectric constant than the bulk dielectric constant of P(VDF-TrFE) copolymer. Because of the surface tension force, the rotation of molecular chains is strongly limited in the interface region. The interface region may also be the result of the Al_2O_3 at the Al electrodes and the Al/P(VDF-TrFE) interface. By plotting the measured reciprocal of unit area capacitance versus the film thickness, it is found that there is a nonzero interception at the zero thickness point, as shown in Figure 2(b). Utilizing a simple series capacitance model, the unit area capacitance C of the film with thickness t can be expressed as

$$\frac{\epsilon_0}{C} = \frac{t}{K_b} + t_s \left(\frac{1}{K_s} - \frac{1}{K_b} \right) \quad (2)$$

where K_b and K_s are the dielectric constant of bulk and interface, respectively, and t_s is the thickness of this interface region. Fitted to Figure 2(b), eq. (2) yields a $K_b = 19$. By assuming that $t_s = 10$ nm, K_s is found to be 4.1, a value close to the dielectric constant of Al_2O_3 .¹⁵

Polarization Response

The polarization hysteresis loops were measured at room temperature on P(VDF-TrFE) 50/50 ultrathin films of varying thicknesses. Typical results of the sample with a thickness of 0.14 μm under various electric fields from 70 to 300 MV/m are shown in Figure 3(a). For films thicker than 0.14 μm , loops that are similar to those in Figure 3(a) (i.e., square and symmetric loops) were observed. However, as the thickness decreased to less than 0.1 μm , the hysteresis loops become lossy and asymmetric. Figure 3(b) shows the results measured on film with a thickness of 72 nm.

As shown in Figure 4(a) and (b), both the remanent polarization (P_r) and coercive field (E_c) increase with the electric field. The polarization shows a saturation trend as the electric field is greater than 300 MV/m, whereas the coercive field remains increasing. As expected, the remanent charges increase with the thickness, whereas the coercive field decreases with the thickness. For example, under an electric field of 150 MV/m, a square hysteresis loop can be ob-

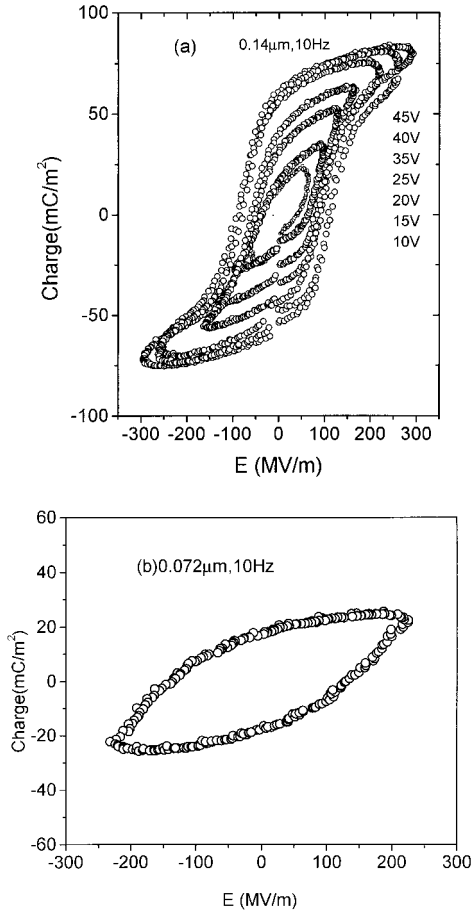


Figure 3 Polarization hysteresis loops for P(VDF-TrFE) 50/50 copolymer ultrathin films measured at different electric fields: (a) 0.14 μm , (b) 72 nm

tained for 0.14 μm film. The E_c of 0.14 μm film is about 75 MV/m, whereas the E_c of 0.3 μm film is about 50 MV/m. The variations of P_r and E_c with thicknesses at 200 MV/m, 10 Hz, are shown in Figure 5(a) and (b). For film with a thickness of 72 nm, there is a drop in polarization, whereas the E_c exhibits a jump, which means the film has less ferroelectricity and more conduction.

As discussed earlier, there is an interface layer between Al electrodes and the P(VDF-TrFE) layer, which has a much lower dielectric constant compared with that of the bulk. This low dielectric constant interface layer could be partially responsible for the observed increase in the coercive field. Using this simple model, an apparent coercive field about 70 MV/m in a film of 0.1 μm thickness (under 100 MV/m electric field) expresses an actual coercive field about 50 MV/m.

Although only the data at 10 Hz were shown in Figures 4 and 5, the hysteresis loops at 1 Hz were

also measured and similar hysteresis loops and variations of charge and coercive field were obtained. The P_r at 1 Hz is higher than that at 10 Hz, whereas the E_c at 1 Hz is a little lower than that at 10 Hz. The results measured on the film with thickness of 0.18 μm are shown in Figure 6(a) and (b). Similar results were observed other films thicker than 0.1 μm .

Effect of Irradiation on the Dielectric and Ferroelectric Properties

Because the coercive field of P(VDF-TrFE) copolymers is extremely high, it is necessary to fabricate these copolymers into thin films for practical uses such as optical and ferroelectric memory elements. However, as discussed in the preceding section, the coercive field will increase as the thickness is reduced. The working voltage is still high, even for a thin film with a thickness of 0.1 μm . In bulk P(VDF-TrFE) copolymers, we observed that high-energy irradiation can signifi-

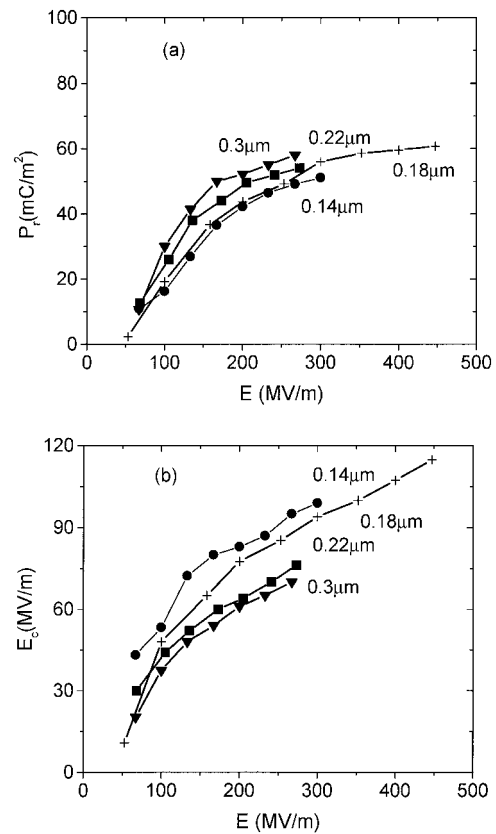


Figure 4 Polarization parameters of P(VDF-TrFE) 50/50 copolymer films of varying thicknesses measured at 10 Hz: (a) remanent charge, (b) coercive electric field.

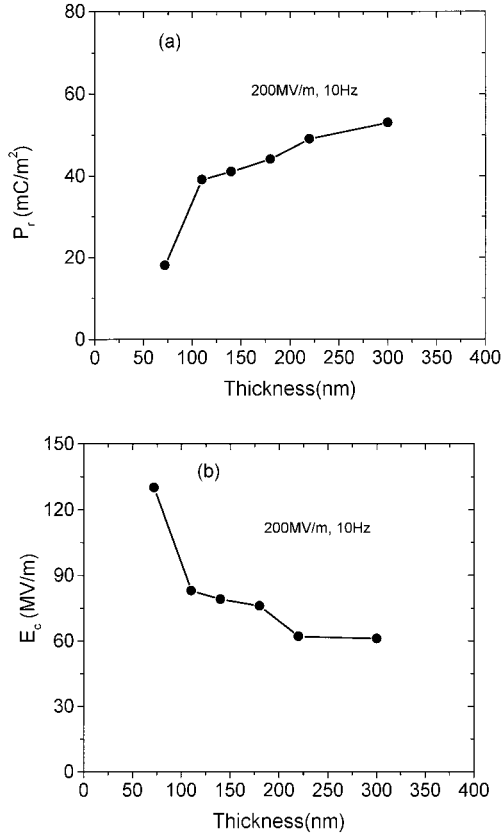


Figure 5 Variation of polarization parameters with thickness under an electric field of 200 MV/m, 10 Hz: (a) remanent charge, (b) coercive electric field.

cantly increase the dielectric constant and reduce the coercive field, which may increase the switching speed.^{16,17}

In ultrathin P(VDF-TrFE) copolymer films, the preliminary experiment of high-energy electron irradiation showed that the irradiation can also significantly modify the polarization hysteresis and the dielectric constant. The results are shown in Figure 7(a) and (b). For the nonirradiated P(VDF-TrFE) 50/50 film with a thickness of 0.11 μm , the coercive field is about 70 MV/m under an electric field of 140 MV/m. After irradiation at 50 Mrad, 95°C, E_c reduced to about 25 MV/m. The dielectric constant at 10 Hz increased from 15 for nonirradiated film to 26 for irradiated film, although the loss increased somewhat.

SEM and X-ray

To understand the effect of thickness on the dielectric properties and polarization behavior, SEM images and X-ray diffraction were measured

on P(VDF-TrFE) 50/50 copolymer ultrathin films. After annealing at 140°C for 2 h, SEM pictures were taken. The identical films were annealed for an additional 24 h and measured again by SEM. Similar results for films annealed at both 2 and 24 h were obtained. A longer annealing time did not significantly increase the crystallinity, although more cracks were observed. Figure 8 shows the SEM images of films with thicknesses of 0.42 μm and 72 nm annealed for 25 h. In thick films (e.g., with thickness of 60 μm), P(VDF-TrFE) crystallized at a temperature above the Curie point, forming lamellate crystallites stacked perpendicular to the film surface.⁶ However, in thin films the copolymer crystallized to form transcrystalline regions, in which crystals grow preferentially normal to the surface. The crystallinity of ultrathin films is less than that of freestanding films. For ultrathin films, the crystallinity decreased with the thickness. As the thickness was reduced to 72 nm, only discontinu-

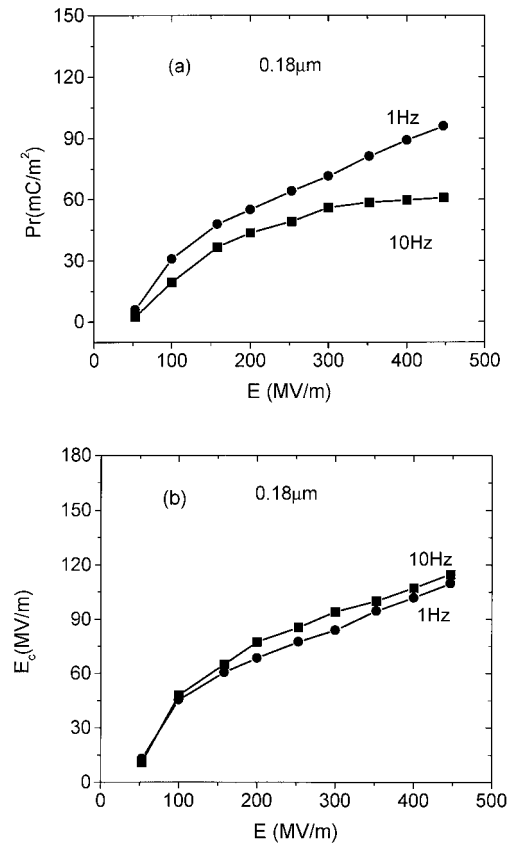


Figure 6 Comparison of polarization parameters at 1 Hz and 10 Hz measured on 0.14- μm film: (a) remanent charge, (b) coercive electric field.

ous dendrite crystals were formed. This provides the explanation for the significant changes in dielectric and ferroelectric properties as the thickness decreased to less than $0.1 \mu\text{m}$.

The X-ray data taken at room temperature from the P(VDF-TrFE) 50/50 copolymer ultrathin films are presented in Figure 9. The data show the evolution of the (200, 110) reflection of the original ferroelectric phase with the thickness. For samples thinner than $0.1 \mu\text{m}$, several scans were carried out to obtain good X-ray data. A two-peak structure at a θ angle near (200, 110) reflection was observed in the thick freestanding P(VDF-TrFE) 50/50 copolymer films in many previous X-ray studies.¹⁸ The peak, centered at $2\theta = 18.9^\circ$ (4.72 \AA), is attributed to the paraelectric-like phase resulting from introduction of conformational changes from T to G and G' . The peak at $2\theta = 19.28^\circ$ (4.59 \AA) results from the ferroelectric β phase packed in *trans*-planar (TTTT) conformation. For ultrathin films, as the thickness de-

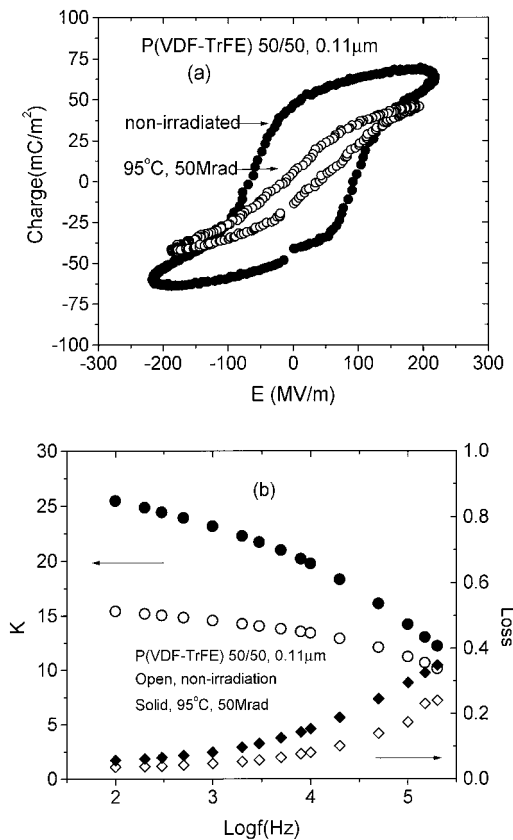


Figure 7 Effect of irradiation on (a) polarization hysteresis loop and (b) dielectric property of P(VDF-TrFE) 50/50 copolymer films with thickness of $0.11 \mu\text{m}$

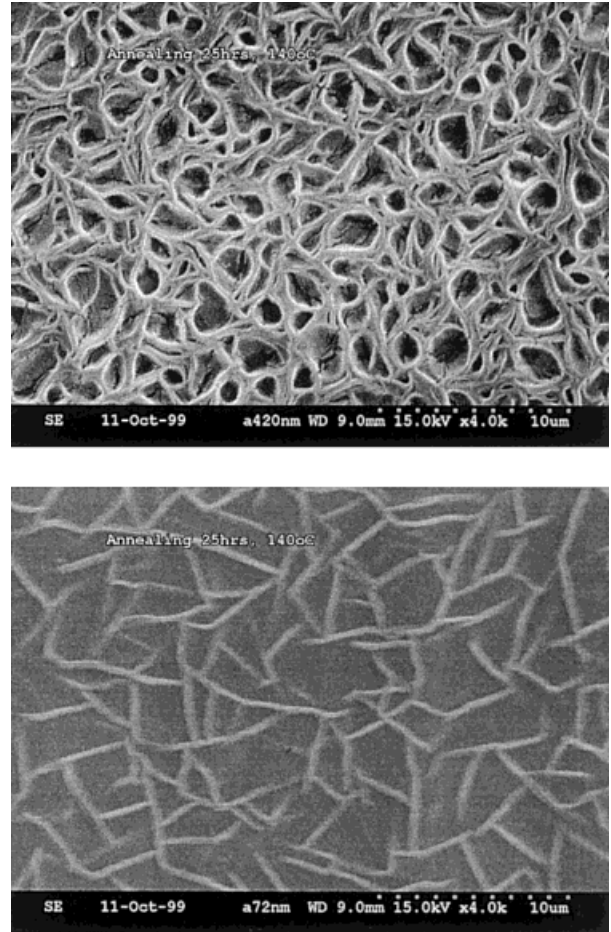


Figure 8 SEM images of P(VDF-TrFE) 50/50 copolymer films with thickness of (a) $0.42 \mu\text{m}$ and (b) 72 nm , annealed at 140°C for 25 h. Similar results were obtained for identical films annealed for 2 h.

creased from 1 to $0.11 \mu\text{m}$, although the intensity of both lower angle and ferroelectric phase decreased, the former reduced significantly, whereas the intensity of the ferroelectric phase still remained high. This is consistent with polarization response. The films with thickness ranging from 0.55 to $0.11 \mu\text{m}$ have similar polarization loops. As the thickness decreased to 72 nm , although the β phase was still observed, it is much lower (note that X-ray diffraction of 72-nm film was scanned seven times to obtain good results). As the thickness decreased even further, the crystallinity of the ferroelectric phase decreased and then disappeared at the thickness of 25 nm .

CONCLUSIONS

The effect of thickness on dielectric properties and polarization behavior of P(VDF-TrFE) 50/50

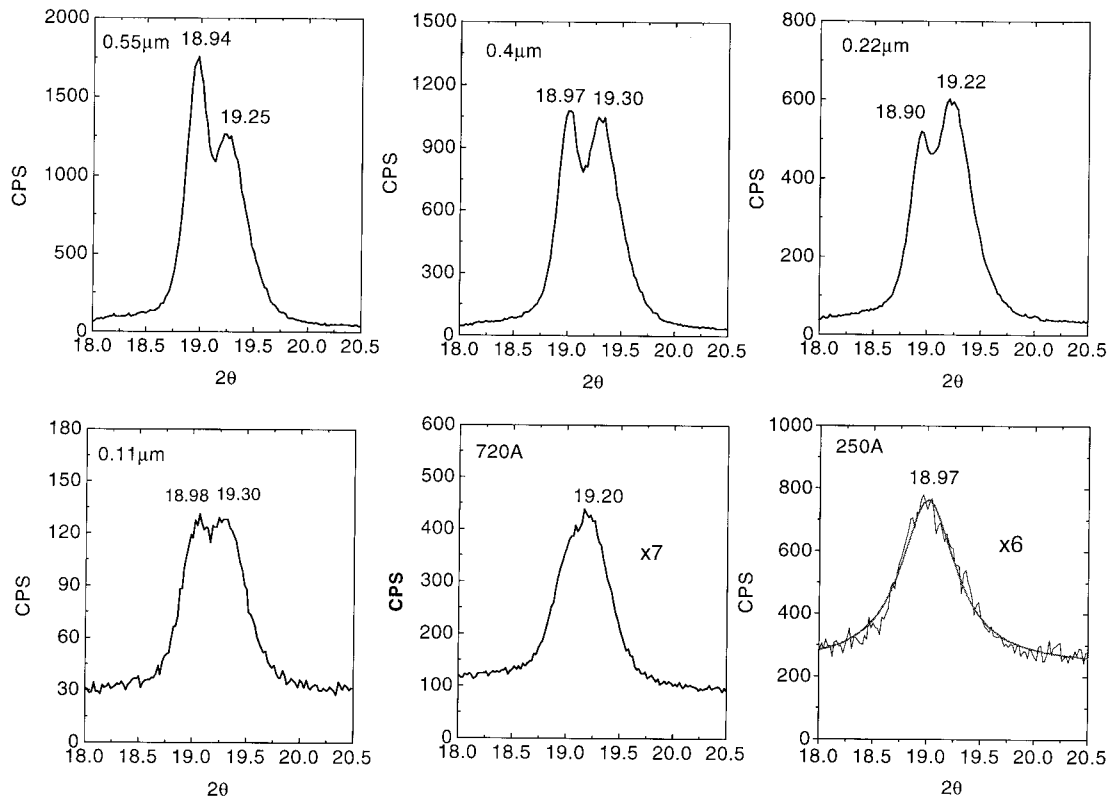


Figure 9 X-ray diffraction of P(VDF-TrFE) 50/50 copolymer films of varying thicknesses.

copolymer ultrathin films, fabricated on silicon wafers covered with platinum by the spin-coating technique, has been investigated. At a thickness less than $0.1 \mu\text{m}$, an abrupt drop of dielectric constant was observed, although there is no significant change in dielectric loss. Above this critical thickness, square and symmetric hysteresis loops were obtained. In contrast, the hysteresis loops of films thinner than $0.1 \mu\text{m}$ were less square. The effect of thickness on dielectric and ferroelectric properties could be explained by the changes of crystal structure in these films and confirmed by SEM and X-ray results. An interface region between the Al electrode and P(VDF-TrFE) was also fitted to interpret the effect of thickness. For ultrathin P(VDF-TrFE) films, irradiation effects on dielectric property and polarization response are similar to those observed in bulk copolymers, which can reduce the coercive field and significantly increase the dielectric constant.

There is still much to be understood about the factors that affect the properties and crystal

structure of P(VDF-TrFE) ultrathin films. These factors include, but are not limited to, the property of the substrate surface, the materials of both bottom and top electrodes, the annealing condition, and the molecular weight and VDF compositions of P(VDF-TrFE) copolymers. Moreover, how to reduce the critical thickness for practical applications remains a challenge.

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