Comparative Investigation of the Structure and Properties of Ferroelectric Poly(vinylidene fluoride) and Poly(vinylidene fluoride–trifluoroethylene) Thin Films Crystallized on Substrates

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) and copolymers of vinylidene fluoride and trifluoroethylene [P(VDF/TrFE)s] were deposited on silicon substrates, and their structure and properties were comparatively investigated. Compared to P(VDF/TrFE), which is the polymer material currently most dominant for ferroelectric thin-film devices applications, our β-phase PVDF homopolymer thin film demonstrated several advantages, such as higher dielectric breakdown strength, improved polarization fatigue endurance, and larger ferroelectric polarization at elevated temperatures with improved thermal stability. The reasons for the observed different characteristics between the PVDF and P(VDF/TrFE) thin films were analyzed on the basis of their different structures and morphologies. The results indicate that the low-cost β-phase PVDF homopolymer thin films have great potential as an alternative to P(VDF/TrFE) for ferroelectric and piezoelectric thin-film-device applications. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3331–3337, 2010

Key words: ferroelectricity; thin films

INTRODUCTION

Strong piezoelectric and ferroelectric effects were first observed in poly(vinylidene fluoride) (PVDF) in the 1970s. In the 1980s, it was found that a synthesized copolymer of vinylidene fluoride and trifluoroethylene [P(VDF/TrFE)] possessed the piezoelectric and ferroelectric properties superior even to that of PVDF homopolymer. Since then, extensive attention has been paid to both PVDF and its copolymers for various device applications on the basis of their ferroelectric and piezoelectric effects.[1,2] Structural studies have shown that PVDF-based polymers have complicated semicrystalline polymorphs (α-, β-, γ-, and δ-crystalline phases). For PVDF homopolymer, the nonferroelectric α phase is most stable thermodynamically. Thus, posttreatments, mainly including mechanical stretching during manufacturing, are required to achieve the most polar β-phase PVDF to obtain the desired properties.[3] On the other hand, P(VDF/TrFE) copolymer with an appropriate vinylidene fluoride content can easily form the β-phase structure, as suggested by theoretical calculation in which the all-trans conformation (the β phase) is most thermodynamically favored for P(VDF/TrFE) with the appropriate vinylidene fluoride content.[4] Thus, PVDF and P(VDF/TrFE) bulk films without substrates possess different characteristics for their device applications: P(VDF/TrFE) can possess excellent ferroelectric and piezoelectric properties without mechanical stretching; PVDF typically has to go through the mechanical stretching process to induce the β phase, but the material cost is significantly lower in comparison to P(VDF/TrFE).

However, as for applications of PVDF-based ferroelectric thin films on substrates, the conventional mechanical stretching process is not applicable for PVDF homopolymer thin films because of the existence of substrates. Thus, P(VDF/TrFE) thin films have predominantly been used in various applications involving substrates, such as tactile sensors[5] and nonvolatile memories.[6] The significantly lower cost and fewer defects in the molecular structure make PVDF homopolymer thin films attractive for replacing P(VDF/TrFE) in many applications. Recently, we succeeded in achieving dense β-phase PVDF homopolymer thin films on silicon substrates without the mechanical stretching process by introducing hydrogen bonds during the thin-film processing,[7,8] and furthermore, these films demonstrated useful ferroelectric and piezoelectric properties.

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Later, there were a few reports on β-phase PVDF homopolymer thin films on substrates.[9,10] However, to the best of our knowledge, there has been no study focusing on the difference in the structure and electrical properties of β-phase PVDF and P(VDF/TrFE) thin films deposited on substrates, which is essential for identifying the strength and weakness of these two materials for device applications and for clarifying the underlying mechanism for the observed different characteristics. Therefore, this study was devoted to a comparative investigation of the PVDF and P(VDF/TrFE) thin films on substrates.

When ferroelectric PVDF and P(VDF/TrFE) thin films with highly related but different molecular structures crystallized under the constraint of substrates, we observed different structural and property features, including ferroelectric fatigue endurance and temperature stability for the two polymer thin films reported here. The relationship between the structure and the performance properties and the advantages of both PVDF and P(VDF/TrFE) were analyzed comparatively with a systematic investigation.

EXPERIMENTAL

We prepared the PVDF and P(VDF/TrFE) (72/28) precursor solutions by dissolving polymers from Sigma–Aldrich and Piezotech S.A., respectively, in a solvent of mixed dimethylformamide and acetone (1:1 by volume). The concentrations of the PVDF and P(VDF/TrFE) solutions were 5 and 10 wt %, respectively. To promote the ferroelectric β phase of PVDF, 0.2 wt % $Mg(NO_3)_2 \cdot 6H_2O$ was introduced to the PVDF solution.[7,8] The corresponding concentration of $Mg(NO_3)_2 \cdot 6H_2O$ in PVDF was 4 wt %. After the polymers were completely dissolved at 50°C for 1 h, the thin films were prepared by spin-coating of the solutions on aluminum-coated silicon substrates. The as-spun films were subsequently dried on a hotplate at 85°C; they were then annealed at 135°C in an oven. The thickness of the thin films was about 1.1 μm for the characterizations of this study, unless specifically defined. Gold layers 300 nm thick were deposited on the films by sputtering with a shadow mask to serve as top electrode layers for electrical measurements. The surface areas of the top electrodes for all of the tested samples were calibrated with an optical microscope.

The crystalline structures were analyzed with an X-ray diffraction (XRD) system (D8-Advance, Bruker AXS GmbH, Karlsruhe, Germany) and Fourier transform infrared (FTIR) spectroscopy (Spectrum 2000, PerkinElmer, USA). The thickness of the films was measured by a surface profiler (Tensor P-10, KLA-Tencor, USA), and the surface morphology was examined with field emission scanning electron microscopy (FESEM; JSM-6700F, JEOL). Polarization/electric field (P–E) hysteresis loops and polarization
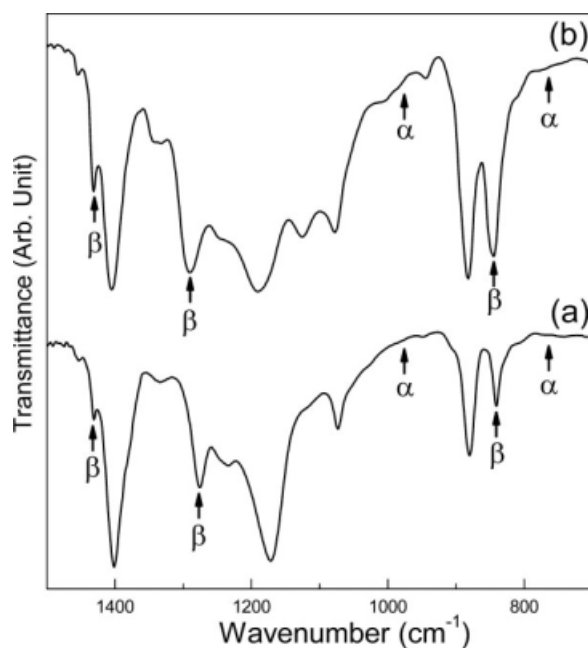

Figure 1 FTIR spectra of (a) PVDF and (b) P(VDF/TrFE) thin films. The arrows indicate the characteristic absorption bands of the α- and β-phase structure. All the unmarked peaks are common to both the α and β phases.

fatigue were studied with a standard ferroelectric testing unit (Precision Premier II, Radiant Technologies) connected to a high-voltage interface. A high-voltage power supply (model 6100, TREK, Inc.) was used for the breakdown strength measurement with a voltage ramp rate of 50 V/min. Before we tested the piezoelectric properties, the films were poled under an electric field of 200 MV/m for 3 min at 100°C. Finally, the piezoelectric coefficient (d_{33}) was measured with a laser scanning vibrometer (OFV-3001-SF6, PolyTech GmbH).

RESULTS AND DISCUSSION

Crystalline structure

The FTIR spectra of the ferroelectric P(VDF/TrFE) film and the PVDF film are shown in Figure 1. Both of the films crystallized into β-phase structures with all-trans conformations with characteristic absorption bands at 844, 1286, and 1431 cm^{-1}.[11,12] The defects in P(VDF/TrFE) introduced by the additional fluorine atoms changed the potential energy of the polymer chains, and the all-trans conformation became a lower energy conformation than that in the TGTG′ form (T = trans; G = gauche) with increasing defect content. As for the PVDF homopolymer, the introduction of the hydrated salts made the all-trans conformation more favorable with the hydrogen bonding between the water of crystallization and the PVDF chains.[7,8] The formation of the β-phase crystalline structure in the films was confirmed by the XRD patterns, as
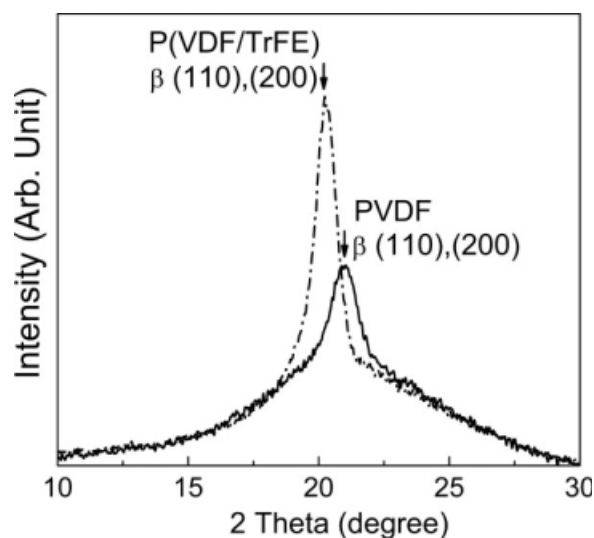
Figure 2 XRD patterns of P(VDF/TrFE) and PVDF thin films.

Figure 3 FESEM images of the surfaces of (a) PVDF and (b) P(VDF/TrFE) thin films.

shown in Figure 2, in which the characteristic diffraction peaks of the β phase at 2θ values of 20.2 and 20.8° were evident for the P(VDF/TrFE) and PVDF films, respectively. The diffraction peak intensity of P(VDF/TrFE) was much higher than that of PVDF and indicated a higher degree of crystallinity of P(VDF/TrFE). During annealing above the Curie point, P(VDF/TrFE) is in hexagonal phase, in which the intermolecular distance expands by 10% and the elastic modulus along the chain direction is reduced by one or two orders of magnitude. As a result, the chains can be very mobile along the chain axes and grow easily to thick lamellar crystals through the sliding diffusion of chain molecules.[13] As for PVDF, the absence of a Curie transition below the melting point might result in much thinner lamellar crystals[14] and, thus, a lower degree of crystallinity.

Surface morphology

Figure 3 presents FESEM images of the P(VDF/TrFE) and PVDF thin films. The surface of the β-phase
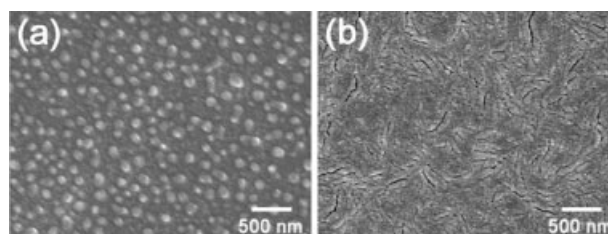
PVDF thin film was dense, with a large amount of tiny granular features on the surface [Fig. 3(a)]. According to our previous study, the tiny granular features were some form of residues from the hydrated salt introduced in the precursor solution.[7] The P(VDF/TrFE) film consisted of crystalline microregions of rodlike shape [Fig. 3(b)], which were composed of multiple stacks of lamellar crystals. We observed that there were large numbers of microgaps or microcracks between the lamellae, which are also typically observed in annealed P(VDF/TrFE) films crystallized on a substrate, as shown in many previous studies.[15-18] The microcavity might have resulted from the tensile stress arising from the volume reduction during the crystallization. Because of the high crystallinity ($\sim$ 80–90%) of the semicrystalline P(VDF/TrFE), as shown in Figure 2, the volume shrinkage accompanied by the crystallization might not have been effectively compensated by the plastic flow of the surrounding amorphous phase, and thus, microcavities formed. This may have been similar to the cavitation occurring during the crystallization of polyethylene.[19] In contrast, the crystallinity of PVDF was only 45–50%, as shown in Figure 2, and thus, less volume reduction and more effective stress relaxation in the amorphous phase led to a dense morphology without the microcavities.

Dielectric properties

The dielectric properties of the ferroelectric P(VDF/TrFE) and PVDF thin films are listed in Table I. The

TABLE I
Summary of the Properties of the PVDF and P(VDF/TrFE) Thin Films

|	Sample	
	PVDF	P(VDF/TrFE)
Dielectric constant at 1 kHz and 25°C	12.5	13.2
Dielectric loss at 1 kHz and 25°C	0.031	0.023
Breakdown strength (MV/m)	524 ± 25	402 ± 25
P_r at 25°C (mC/m^2)	84.1	83.5
Coercive field at 25°C (MV/m)	115	68
P_r at 110°C/P_r at 25°C	1.19	0.56
Polarization fatigue endurance (cycles to 75% of P_r)	5.6×10^4 (100 Hz) and 2.7×10^5 (5 kHz) at 350 MV/m	6.5×10^3 (100 Hz) and 2.1×10^5 (5 kHz) at 150 MV/m
d_{33} effective on the substrate (pm/V)	−15.0	−17.8
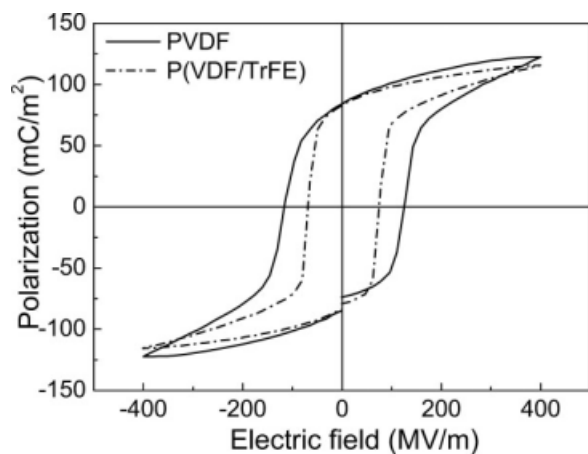
Figure 4 P–E hysteresis loops for P(VDF/TrFE) and PVDF thin films.

polymer thin films exhibited comparable dielectric constant and loss properties. However, the breakdown strength of the β-phase PVDF thin film (524 MV/m) was substantially higher than that of P(VDF/TrFE) (402 MV/m). We believed that the microcavities, as observed in Figure 3(b), did deteriorate the dielectric strength of P(VDF/TrFE).

Ferroelectric properties and temperature stability

The P–E hysteresis loops of the P(VDF/TrFE) and PVDF thin films are shown in Figure 4. The remnant polarization (P_r) of the β-phase PVDF thin film was 84.1 mC/m^2, and the coercive field was 115 MV/m. The value of P_r was similar to that of our P(VDF/TrFE) film and also those of the P(VDF/TrFE) thin films on substrates reported in the literature.[20] However, the coercive field for the PVDF film was considerably higher than that of the P(VDF/TrFE) thin film.

If we only took into account that P_r originated from the ferroelectric β-phase crystals, the P(VDF/TrFE) film with the higher crystallinity of the β phase should have exhibited a substantially higher P_r than that of the PVDF film. However, the CHF—CF$_2$ units in the P(VDF/TrFE) copolymer could have significantly reduced the electric polarity in comparison to the CH$_2$—CF$_2$ units in the homopolymer chains. According to a recent theoretical study, the polarity of a perfect β-phase PVDF crystal is about 1.45 times as high as that of perfect P(VDF/TrFE) crystal with a vinylidene fluoride/trifluoroethylene ratio of 72/28.[21] Therefore, there is a trade-off between enhanced crystallinity and weakened polarity in P(VDF/TrFE), both of which are caused by the existence of a high content of molecular defects (CHF—CF$_2$ units). This could explain the fact that our β-phase PVDF homopolymer thin film exhibited a P_r value similar to that of P(VDF/TrFE), despite its significantly lower crystallinity.

To evaluate the thermal stability of the ferroelectric properties of the P(VDF/TrFE) and PVDF thin films, their P–E hysteresis loops were measured at different temperatures, and the results are given in Figure 5(a,b), respectively. The thickness of the film samples shown in Figure 5 were 0.40 μm; this was smaller than that of the samples shown in Figure 4 to obtain the adequately large electric field required for effective fatigue characterization with voltage
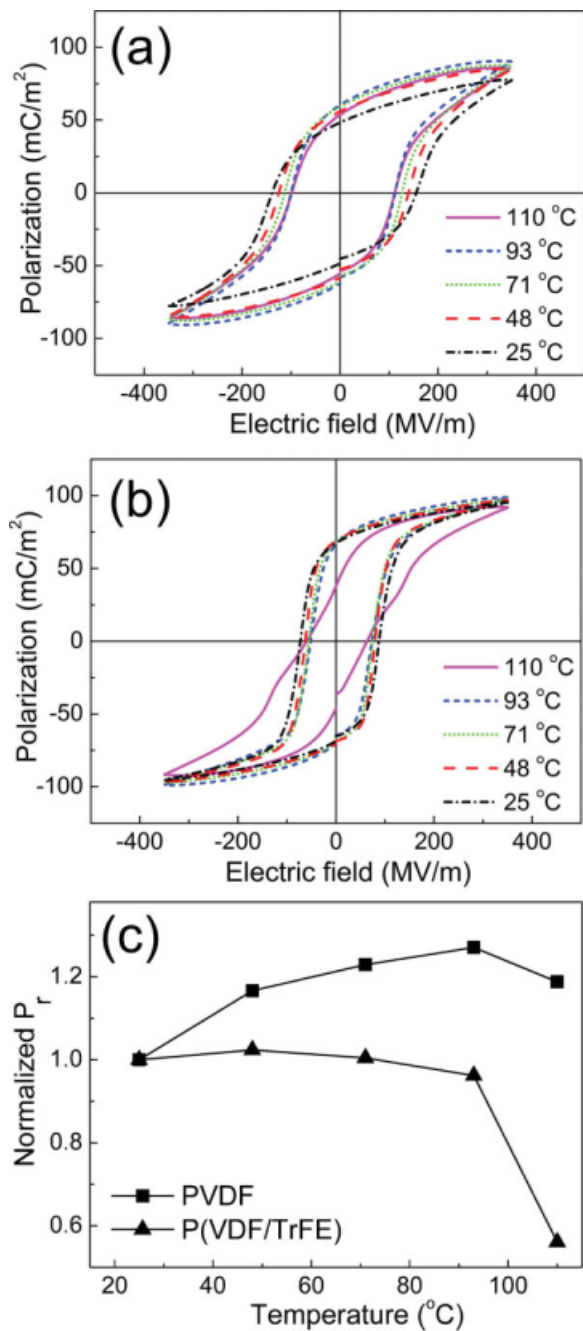

Figure 5 (a,b) P–E hysteresis loops at different temperatures for PVDF and P(VDF/TrFE) thin films, respectively, and (c) normalized P_r versus the temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

magnitude available in the standard fatigue characterization mode in the system. The temperature dependences of the normalized P_r values for the P(VDF/TrFE) and PVDF thin films are compared in Figure 5(c). With increasing temperature up to 110°C, the β-phase PVDF thin film exhibited an increase in P_r, accompanied by a substantial reduction in the coercive field. In contrast, the P_r values of the P(VDF/TrFE) thin film decreased slightly with increasing temperature; this was followed by significant drop to 56% at 110°C compared to that tested at 25°C.

The dipoles in ferroelectric polymers should possess a higher mobility at elevated temperatures; this led to a reduction in the large coercive field of PVDF and the enhancement of P_r. It has also been shown recently that, in semicrystalline ferroelectric polymers such as PVDF, the charges necessary for compensating and stabilizing the polarization of the crystallites are very important for obtaining a stable polarization,[22–24] and there should have been more charges injected into PVDF with a higher mobility at a higher temperature to stabilize the polarization. In contrast, P_r of P(VDF/TrFE) was not improved with increasing temperature as the dipoles might have been effectively switched and stabilized even at room temperature. The drop in P_r of P(VDF/TrFE) at 110°C was due to the fact that the temperature approached its Curie temperature.[25,26] As PVDF does not have a Curie temperature until its melting point of about 170°C, it did not show any significant drop in P_r at 110°C.

Fatigue behavior

The fatigue behavior of ferroelectric polymer thin films is crucial to many device applications, particularly for ferroelectric memories. In our fatigue characterization, a higher electric field of 350 MV/m was applied to the PVDF thin film because it had a large coercive field and a high dielectric strength, whereas a lower electric field of 150 MV/m was applied to the P(VDF/TrFE) thin film. Figure 6 shows the comparison of the P_r degradation of the P(VDF/TrFE) and PVDF thin films under alternating-current (ac) electric fields of 150 and 350 MV/m, respectively. Both films exhibited a big drop in P_r after certain cycles of switching, but PVDF showed improved fatigue endurance, even when a much larger electric field was applied. When the film was driven at 100 Hz, the P_r of the P(VDF/TrFE) thin film dropped to 75% of its initial value after 6.5×10^3 cycles, which was comparable to the fatigue behavior of a P(VDF/TrFE) thin film reported by Zhu et al.[27] In contrast, the P_r of the PVDF thin film dropped to 75% of its initial value only after 5.6×10^4 cycles. At higher driving frequencies, the polarization fatigue endurance of the two polymer films differed only slightly.

At 5 kHz, the P_r of the P(VDF/TrFE) and PVDF thin film dropped to 75% of the initial value after 2.1×10^5 and 2.7×10^5 cycles, respectively. The improved polarization fatigue endurance of PVDF over P(VDF/TrFE) could have resulted from its dense morphology in contrast to the existence of a large number of cavities in P(VDF/TrFE), as shown in Figure 3. Most of the P(VDF/TrFE) films could not sustain the ac electric field of 350 MV/m as applied to the PVDF thin films. Under the ac field, the discharge could have happened much more easily because of the quick diminish of charges under an inversed electric field.[28]

Piezoelectric properties

The P(VDF/TrFE) and PVDF thin films were poled, and their piezoelectric properties were evaluated by a reliable method[29] with a laser scanning vibrometer.
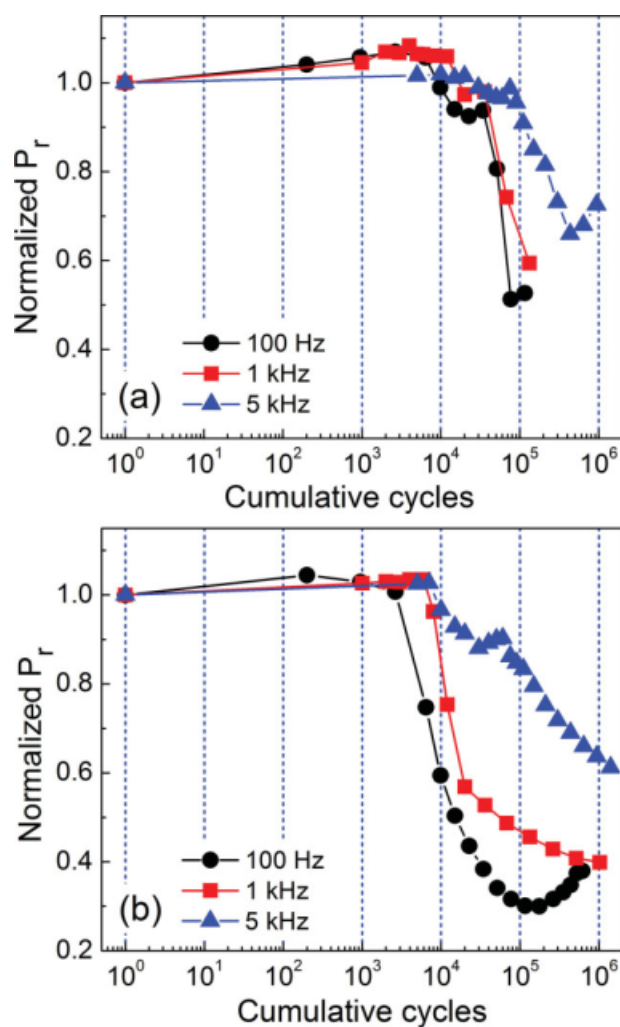

Figure 6 Change in P_r under the cycling of a large ac electric field: (a) a PVDF thin film under 350 MV/m and (b) a P(VDF/TrFE) thin film under 150 MV/m. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
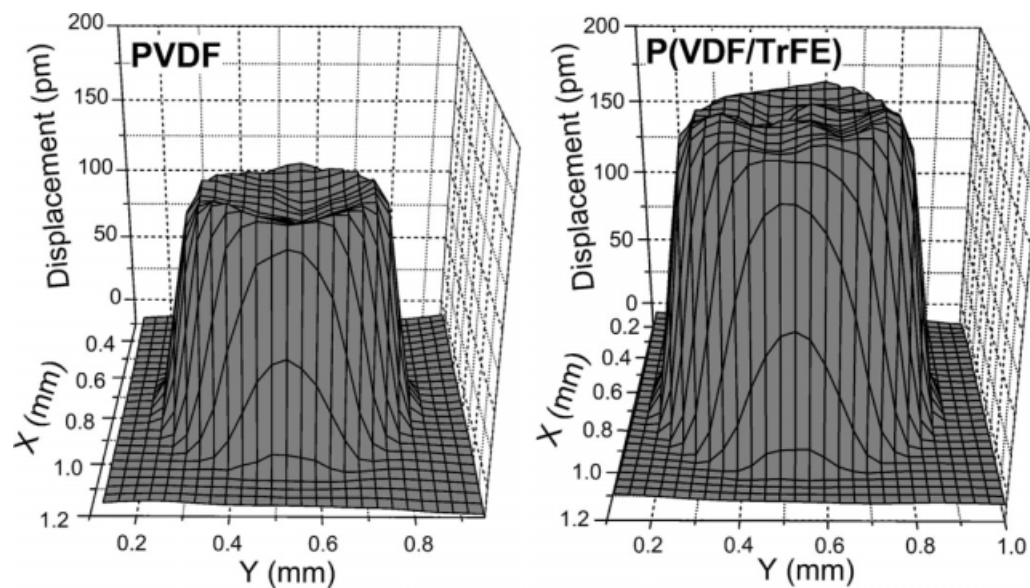
Figure 7 Three-dimensional drawings of the instantaneous vibration data when the displacement magnitude of the polymer films reaches the maximum in the sine-wave electric driving (amplitude = 10 V, frequency = 10 kHz).

Figure 7 presents three-dimensional drawings of the instantaneous vibration data for when the displacement magnitude of the polymer films reached the maximum in the sine-wave electric driving. The central protruding area is the electrically excited area under the gold electrode, whereas the flat surrounding area is the polymer film not covered by any top electrode. During the testing, a unipolar ac signal of 10 V (amplitude) at 10 kHz was applied to the samples. The effective d_{33} value of the P(VDF/TrFE) and PVDF thin films were -17.8 and -15.0 pm/V, respectively, without any clamping effect of the substrate taken into account.[29]

In consideration of the strong constraint of the rigid substrate to the significantly softer polymer film, the actual d_{33} value should have been significantly larger than the value determined. To evaluate the actual d_{33} value of the polymer thin films, a numerical simulation was conducted by the finite element method (FEM) with commercial software (Abaqus CAE version 6.22, SIMULIA, Providence RI). On the basis of the simulation results and with the elasticity values of the polymer thin film, top and bottom electrodes, and substrate taken into account, the actual d_{33} values of the P(VDF/TrFE) and β-phase films were determined to be -34.0 and -31.2 pm/V, respectively; these values were comparable with those of uniaxially stretched bulk PVDF and P(VDF/TrFE) membranes without a substrate.[30,31] All of the major dielectric, ferroelectric, and piezoelectric properties, including ferroelectric fatigue endurance and temperature stability, for both the PVDF and P(VDF/TrFE) polymer thin films are summarized in Table I for comparison.

CONCLUSIONS

The structure and properties of ferroelectric P(VDF/TrFE) copolymer and PVDF homopolymer thin films deposited on silicon substrates were comparatively investigated. The PVDF thin films exhibited a dense morphology with a relatively lower crystallinity of the ferroelectric β phase, whereas the P(VDF/TrFE) thin films were characterized with the existence of microcavities but a high crystallinity of the β phase. The high degree crystallinity of the P(VDF/TrFE) films led to a lower coercive field and a slightly larger piezoelectric coefficient. However, compared to P(VDF/TrFE), the PVDF thin films exhibited higher dielectric breakdown strengths and improved polarization fatigue endurance because of their denser morphology and also their superior thermal stability at elevated temperatures. Despite their lower crystallinity, the β-phase PVDF thin films showed a ferroelectric P_r value similar to that of P(VDF/TrFE) because of the intrinsic high polarity in the molecular structure of the PVDF homopolymer. The results indicate that the low-cost β-phase PVDF homopolymer thin films have great potential as an alternative to P(VDF/TrFE) for ferroelectric and piezoelectric thin-film-device applications.

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