Huge electrocaloric effect in Langmuir–Blodgett ferroelectric polymer thin films

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Abstract. In this work, we studied polyvinylidene fluoride (PVDF)-based ferroelectric copolymer and terpolymer films grown, by the Langmuir–Blodgett (LB) technique, on polyimide substrates. The LB technique is believed to improve the film quality, i.e. to confer better crystallinity and less parasitic amorphous phase. As a consequence, a reversible adiabatic temperature change ΔT up to 21 K is demonstrated. The large electrocaloric effects of LB films close to room temperature suggest the potential for applying LB films in cooling systems.

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1. Introduction

Owing to their high chemical stability, excellent flexibility and compatibility with lithographic and physical patterning techniques, ferroelectric polymers have appealing advantages when integrated into semiconductor devices. Among them, polyvinylidene fluoride (PVDF)-based ferroelectric copolymers with trifluoroethylene (TrFE) and chlorofluoroethylene (CFE) are most investigated because of their strong pyroelectricity, huge energy density and huge electromechanical responses [1]–[4]. Recently, the huge electrocaloric effect (ECE) resulting from changes in the entropy and temperature of a material under an applied electric field has attracted the attention of researchers to ferroelectric materials [5]. The ECE occurs in both ferroelectric and paraelectric phases, and is found to be larger in the paraelectric phase just above the ferroelectric–paraelectric phase transition [6].

In a working cycle-based ECE, the working material contacts the load and absorbs entropy from it. Then the material is isolated from the load and an electric field is applied. With an increase in the electric field, the polarization and temperature of the working material increase under adiabatic condition. The material is then placed in thermal contact with the heat sink and transfers the entropy absorbed from the load to the heat sink. Then the material is isolated from the heat sink. As the applied field is reduced, the temperature of the material decreases back to the temperature of the cooling load. Thus, the larger the ECE of the working material, the better the efficiency of cooling.

Indeed the ordering and disordering of dipoles in PVDF-based copolymers can result in a large entropy change, which has been confirmed by Neese et al [7, 8]. However, because of a rather large amount of parasitic amorphous phase (typically >25 wt%) existing in their films, the experimental values of the measured ECE are 15–25% lower than those theoretically predicted [7]. It is well known that the Langmuir–Blodgett (LB) technique allows us to fabricate high-quality, excellent-crystalline and huge-breakdown-voltage copolymer P(VDF-TrFE) thin films [9]–[12]. Our previous investigation has demonstrated that good crystallinity, highly planar ordered and close parallel packing of the molecules in LB polymers lead to large electric tunability [13]. As a consequence, it is reasonable to believe that such a growth process will also improve the ECE of PVDF-based films.

In this paper, we present a detailed investigation of the ECE of P(VDF-TrFE) and P(VDF-TrFE-CFE) films grown, by the LB technique, on technologically desirable aluminized flexible polyimide substrates. Our results clearly show a large ECE, as the variations of adiabatic temperature $\Delta T$ of P(VDF-TrFE) films (at 390 K under 300 MV m$^{-1}$) and P(VDF-TrFE-CFE) films (at 350 K under 350 MV m$^{-1}$) are $\sim$21 K.

2. Experimental

Copolymers of P(VDF-TrFE) films with a VDF/TrFE molar ratio of 70:30 and terpolymers of P(VDF-TrFE-CFE) with a VDF/TrFE/CFE molar ratio of 56.2:36.3:7.6 are therefore fabricated by horizontal LB technology, namely Langmuir–Schaefer horizontal deposition [14, 15]. Solutions are prepared with a concentration of about 0.05 wt% in dimethyl sulfoxide. The surface pressure of deposition impacts the physical properties of LB films [16, 17]. In order to determine the optimal magnitude of surface pressure for monolayer deposition on the polyimide substrate surface, the surface pressure versus area per molecule isotherm is studied in figure 1. This shows that the area of the molecule unit coincides with the calculated
value 5.7 Å\(^2\) [18] at a surface pressure of about 5 mN m\(^{-1}\). This indicates that a well-compacted monolayer appears on the subphase at 5 mN m\(^{-1}\). This result is similar to the report of Palto et al [18]. According to decrement of the area occupied by a monolayer in the water surface and the area of the solid substrate, the average magnitude of deposition ratio \(k\) is 0.98, which suggests good film homogeneity.

The films are transferred at a surface pressure of 5 mN m\(^{-1}\) and consist of 50 deposition layers. On the basis of variable-angle spectroscopic ellipsometry analysis, the thickness of one deposition layer is basically two or three times the molecular diameter, whose thickness is about 1.78 nm, in agreement with the results of Ducharme et al [15]. The total thickness of our films with 50 layers is therefore about 90 nm. In order to improve the properties, these films were annealed at 407 K for 5 h. Aluminum is evaporated onto the P(VDF-TrFE) film to form the capacitor structure, which is then annealed at 397 K for 2 h. The temperature dependence of dielectric constants is measured using an Agilent E4980A impedance analyzer with an ac drive voltage of 0.02 V in a 60 K temperature range (340–400 K for P(VDF-TrFE) copolymers or 280–340 K for P(VDF-TrFE-CFE) terpolymers) with a rate of 2 K min\(^{-1}\). The frequency is varied from 1 to 100 kHz. High-resolution x-ray measurements were performed on a highly accurate two-axis diffractometer in a Bragg–Brentano geometry with Cu-K\(\alpha\) wavelength issued from an 18 kW rotating anode generator. The polarization versus electric field (\(P–E\)) hysteresis loops are measured using a Radiant Precision LC system at 1 kHz and at various temperatures upon heating. The specific heat data were taken using a Perkin Elmer DSC-2C differential scanning calorimeter.

3. Results and discussion

Figure 2 shows x-ray diffraction measurements on both samples. For P(VDF-TrFE) films, the paraelectric \(\alpha\)-phase is present above 390 K. Below 390 K, there is a mixture of \(\alpha\)-phase and ferroelectric \(\beta\)-phase. This is a clear characteristic of the structural change in P(VDF-TrFE) films that accompanies the phase transition. For relaxor P(VDF-TrFE-CFE) films, only one peak exists at any temperature below the melting transition temperature. These
results are consistent with temperature dependence of dielectric constant in figure 3. Whereas the ferroelectric–paraelectric (P–P) phase transition corresponding to the maximum of the dielectric constant occurs near \( T_c \sim 388 \text{ K} \) for P(VDF-TrFE) films (inset of figure 3(a)), for P(VDF-TrFE-CFE) films, the broad dielectric constant peak exhibits a relaxor behavior as its position shifts to higher temperature with frequency and does not correspond to any transition (inset of figure 3(b)).

The \( P–E \) loops measured at 1 kHz on P(VDF-TrFE) copolymers in the temperature range from 390 to 410 K and on P(VDF-TrFE-CFE) terpolymers in the temperature range from 300 to 350 K are presented in figure 3. Reversible adiabatic temperature changes \( \Delta T \) due to an applied electric field \( E \) are given by \[ \Delta T = -\frac{1}{\rho} \int_{E_1}^{E_2} T \frac{\partial P}{\partial T} \frac{\partial S}{\partial E} \text{d}E, \] assuming the Maxwell relation \( \frac{\partial P}{\partial T} = \frac{\partial S}{\partial E} \). Figure 4 shows the value of heat capacity \( C_p \). For P(VDF-TrFE-CFE), there is no heat capacity peak in the temperature range of the dielectric constant peak, which is consistent with the characteristic of the ferroelectric relaxor. However, the heat capacity peak of P(VDF-TrFE) that results from the F–P transition appears close to 373 K, which is 15 K lower than that of the dielectric constant peak. A similar experimental phenomenon has been observed by Zhang et al [20]. Two effects can cause a discrepancy in phase transition temperature between the dielectric constant and the specific heat for P(VDF-TrFE). Firstly, the step of temperature is 5 K in specific heat measurement, which may lead to imprecise temperature versus peak. Secondly, the specific heat is measured from the P(VDF-TrFE) copolymer that is under stress-free condition. However, the dielectric constant is obtained from copolymer films that are subjected to the mechanical constraint of the substrate. Previous theoretical calculation has shown that the misfit strains can change the phase transition temperature of copolymer films [21].

ECE temperature changes obtained by equation (1) are presented in figure 5. It can be found that the largest change \( \Delta T \) of P(VDF-TrFE) and P(VDF-TrFE-CFE) is 21.2 K (at 390 K
under a 300 MV m\(^{-1}\) electric field) and 21.6 K (at 350 K under a 350 MV m\(^{-1}\) electric field), respectively. Comparing our results of \(\Delta T\) with the previous best results [7] in the same electric field, our experiments obtained much better values, as \(\Delta T\) is equal to 13.5 K for P(VDF-TrFE) at 200 MV m\(^{-1}\) and 18.4 K for P(VDF-TrFE-CFE) at 300 MV m\(^{-1}\). The higher F–P phase transition temperature and fewer defects may be responsible for the increase of ECE.

The phenomenological calculation of the stress-free P(VDF-TrFE) copolymer is presented in figure 6. The thermodynamic potential \(G\) as a function of polarization \(P\) and applied field \(E\) is given by

\[
G = G_0 + \alpha_0 (T - T_0) P^2 + \beta_0 P^4 + \gamma P^6 - EP,
\]

(2)

where \(\alpha_0\), \(\beta_0\) and \(T_0\) result from [7, 8]. The sixth-order polarization terms in the free energy are neglected. Taking into account the equilibrium condition \(\partial G / \partial P = 0\), one can obtain \(E = \alpha_0 (T - T_0) P + \beta_0 P^3\). Differentiating \(E\) with respect to \(T\) and solving equation (1), we can
Figure 4. Specific heat for P(VDF-TrFE) copolymers and P(VDF-TrFE-CFE) terpolymers.

Figure 5. Polarizations from $P-E$ loops and adiabatic temperature change $\Delta T$ versus temperature in different electric fields for (a) P(VDF-TrFE) films and (b) P(VDF-TrFE-CFE) films.
obtain temperature dependences of adiabatic temperature change $\Delta T$ in different electric fields. Because of the strong change of $\alpha_0$ with temperature in P(VDF-TrFE-CFE) terpolymers [8], it is difficult to calculate $\Delta T$ by the phenomenological model. Nevertheless, in the case of P(VDF-TrFE) copolymers, figure 6 shows that the maxima of $\Delta T$ are $\sim 15.5$ and $\sim 24$ K in 200 and 300 MV m$^{-1}$ fields, respectively. Our experimental values are still weaker than those of the theoretical prediction, which can be attributed either to a small amount of amorphous phase and/or defects in our LB films or to the simplicity of the phenomenological model used. Although previous research [22]–[24] has demonstrated the existence of little $\alpha$-like phase clusters or defects in LB films, ferroelectric copolymer films fabricated by the LB technique are believed to possess better crystallinity. Note that defects or amorphous phase can pin the domain motion under high electric fields for P(VDF-TrFE) copolymers. Owing to better crystallinity, fewer defects and amorphous phase, the temperature dependence of polarization, i.e. the pyroelectric response, is improved in the LB copolymer films. It is well known that ECE is a reversible process of the pyroelectric response. Therefore high crystallinity, fewer defects and amorphous phase lead to enhancement of the ECE. For LB terpolymer P(VDF-TrFE-CFE) films, although there is no macroscopic domain, the nanopolar regions (nanometer-size all-trans ferroelectric chains) may grow under high electric fields if the applied electric field is high enough to overcome the barriers for the nanopolar regions to grow. In addition, since the relaxor ferroelectric terpolymers exhibit large electrostriction, high electric fields can result in significant strains, which may influence the orientation of the molecules [25, 26]. As a result, through the coupling between the strains and the orientation of the molecules, high electric fields may make more molecules align along the electric fields, which results in a larger change of polarization with temperature.

4. Conclusions

In summary, we have demonstrated a large ECE in LB P(VDF-TrFE) copolymer films and P(VDF-TrFE-CFE) terpolymer films. The maxima of adiabatic temperature change $\Delta T$ are

Figure 6. Adiabatic temperature change $\Delta T$ for P(VDF-TrFE) films in different electric fields derived from phenomenological theory.
∼21 K both at 390 K (under 300 MV m⁻¹) for P(VDF-TrFE) copolymers and at 350 K (under 350 MV m⁻¹) for P(VDF-TrFE-CFE) terpolymers, respectively. Especially for P(VDF-TrFE-CFE) terpolymer films, the peak of ΔT is close to room temperature. Considering their practical availability, ferroelectric PVDF-based polymers are potentially applicable for refrigeration by ECE.

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