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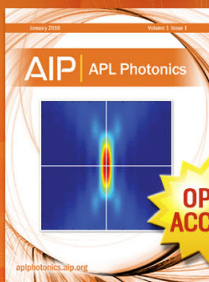
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Irreversible extinction of ferroelectric polarization in P(VDF-TrFE) thin films upon melting and recrystallization

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We observed the irreversible extinction of ferroelectric polarization in spun coated poly(vinylidene fluoride-co-trifluoroethylene) thin films upon melting and recrystallization. We investigate the alteration of the ferroelectric properties correlated with the preferred polymer crystal orientation with respect to the electrodes using grazing incident scattering, spectroscopy, and electron microscopes. Heat treatment above melting point gave rise to the significant reduction of the ferroelectric performance mainly caused by the modification of molecular orientation of polymer crystals whose *c* and *b* axes are perpendicular and parallel to the electrode surface, respectively, leading to almost zero effective electric field. © 2006 American Institute of Physics.

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With the tremendous demand for an electrically addressable memory technology that can be placed into organic integrated circuits,¹ ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) P(VDF-TrFE) copolymers were often introduced to have possibilities of application for the nonvolatile and low cost memory device.^{2,3} A number of studies⁴⁻⁹ have been focused on the ferroelectric behavior; permanent polarization,^{4,5} switching time,⁶ coercive voltage,⁷ crystallinity in ultrathin films,⁸ interfacial layer control of ferroelectric capacitors,⁹ and electroactive polymers irradiated by electron beam.^{10,11} For both low voltage switching below 5 V and low fabrication cost, the polymer should be solution processed with the film thickness of less than 100 nm due to its high coercive field (E_c) of approximately 50 MV/m. The efforts to reduce the film thickness for the device operating at low voltage encounter the difficulties that there exists the threshold film thickness below which polymer capacitors have dramatically low crystallinity and consequently increase the switching time.¹² For overcoming these problems, many researchers have concentrated on the issues of increasing crystallinity¹³ and/or controlling crystal orientation.¹⁴ Thermal treatment including the process of consecutive annealing has been considered to be one of the most effective processes so as to enhance the ferroelectric properties.¹⁵ However, most works have been focused on the effect of annealing temperature in the range of Curie (T_C) and melting temperature (T_m). In order to adopt the polymer ferroelectrics into the current integrated process which requires high tem-

perature well above T_m , the ferroelectric properties become more important, depending on thermal history from melt recrystallization.

Here we present the effect of thermal treatment of thin P(VDF-TrFE) films on ferroelectric properties. The improved remnant polarization observed in the samples annealed at temperatures between T_C and T_m completely disappears when the samples are heated above T_m and recrystallized through various pathways. Extinction of the remnant polarization of the melt-recrystallized samples arises from the modification of the molecular chain orientation upon recrystallization presumably due to the preferential crystal face interaction to the electrode surface.

We employed a P(VDF-TrFE) copolymer with 27.5% TrFE which was kindly supplied from MSI Sensor, PA, USA. The crystallinity index calculated from the experimental melting enthalpy and the equilibrium enthalpy of a perfect crystal of PVDF (104.7 J/g) was nearly 60%. T_m and T_C of P(VDF-TrFE) were 150 and 80 °C, respectively. Thin film formation was done by spin coating with 1%–3% P(VDF-TrFE) solution in methyl ethyl ketone (MEK). Thickness of the fabricated film was measured by ellipsometry (Gaertner Scientific Co. USA). Heat treatment for the films was performed on the heating stage (Linkam 600, UK) with different steps demonstrated in Fig. 1(a). Metal/P(VDF-TrFE)/metal capacitors were made with highly doped silicon (100) substrate as the bottom electrode. Aluminum top electrodes were evaporated on polymer films using a shadow mask with holes of 200 μm in diameter under a pressure of $\sim 10^{-6}$ mbar and a rate of ~ 0.1 nm/s. Ferroelectric properties were obtained using a RT66A unit (Radiant Technolo-

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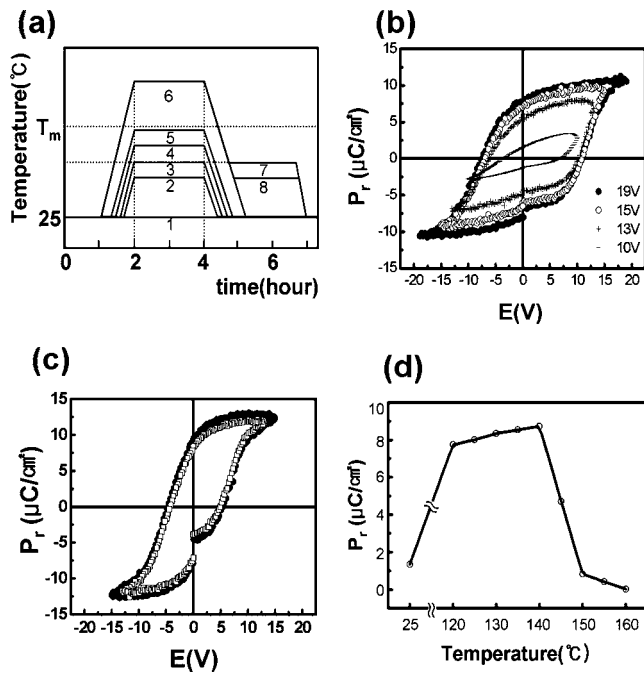


FIG. 1. (Color online) (a) Various routes for annealing treatments as a function of time. Each film was experienced thermal annealing treatment at different temperatures via the routes of 1–8. (b) Polarization P vs applied voltage E hysteresis loops of a P(VDF-TrFE) polymer capacitor. (c) Ferroelectric hysteresis loops of a 70 nm thin P(VDF-TrFE) polymer film. (d) The remnant polarization (P_r) as a function of annealing temperature.

gies). The structures of the films were characterized by scanning electron microscope (SEM, HITACHI S-2700), transmission electron microscope (TEM, Phillips X60), and the grazing-incidence x-ray diffraction (GIXD). Infrared grazing-incidence reflection absorption spectra (GIRAS) were collected using Bruker-IFS66V spectrometer.

Figure 1(b) shows a typical hysteresis loop of 200 nm P(VDF-TrFE) film spun coated from 3 wt % solution and annealed at 120 °C for 2 h. The remnant polarization (P_r) and coercive voltage (V_c) in a saturated curve are approximately $7.8 \mu\text{C}/\text{cm}^2$ and 11 V corresponding to coercive electric field (E_c) of approximately 50 MV/m, when the applied voltage is above ± 15 V, which is consistent with that reported by others.^{4,9} The very low switching voltage of 4.9 V was detected in the 70 nm film [Fig. 1(c)]. Further lowering the thickness caused the significant reduction of the polarization due to the reduced crystallinity.

The polarization increased slightly with the annealing temperature before crystal melting, as shown in Fig. 1(d). Heat treatment of the samples above T_m dramatically reduced the remnant polarization irrespective of the pathways of recrystallization: one rapidly cooled to room temperature (sample 6), others slowly cooled with the rate of $2^\circ\text{C}/\text{min}$, to 120 and 130 °C and annealed at each temperature for 2 h (samples 7 and 8, respectively), as shown in Figs. 1(a) and 1(d). The similar extinction of the polarization was also observed even in thinner films.

In order to understand the abnormal ferroelectric behavior of the thin film which underwent the melting and recrystallization, we have performed GIXD which provides us the information of both degree of crystallization and molecular orientation. Figure 2 shows a series of two-dimensional (2D) GIXD patterns of thin P(VDF-TrFE) films obtained after heat treatment with the routes illustrated in Fig. 1(a). The

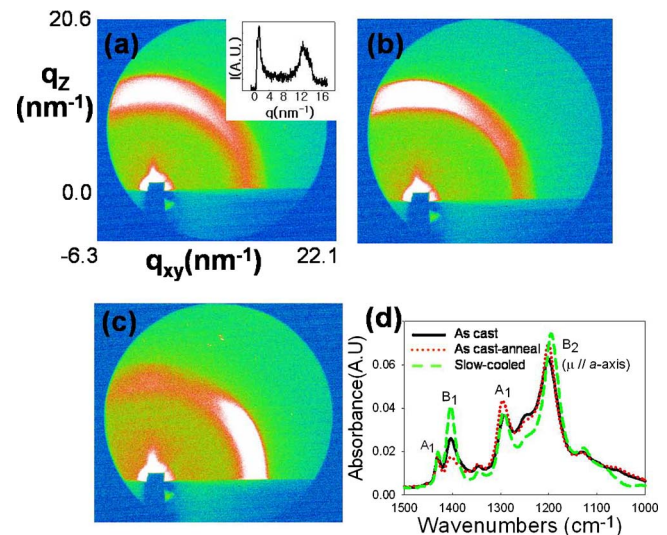


FIG. 2. (Color online) 2D GIXD patterns and GIRAS spectra for P(VDF-TrFE) thin films with different annealing treatments: (a) as-cast films, (b) at 120 °C, (c) at 170 °C, and (d) GIRAS spectra. Inset of (a) displays an intensity profile along the vertical (meridian) direction.

patterns from the as-cast film [Fig. 2(a) and inset] and the annealed one at 120 °C [Fig. 2(b)] display the arced strong reflection near $q = 12 \text{ nm}^{-1}$ ($q = 4\pi \sin \theta / \lambda$) with twofold symmetry on the meridian which corresponds to both $\{110\}$ and $\{200\}$ reflections of orthorhombic P(VDF-TrFE) crystals. The orientation of the reflections arose from the preferential crystal orientation in which the c axis, molecular chain axis, is preferentially aligned parallel to the substrate surface by the strong bias centrifugal force field generated during spin coating. In this situation, both a and b axes can rotate around the c axis randomly. The external electric field applied in the polarization measurement induces the preferential orientation of the polar b axis towards the electric field direction irreversibly, which is responsible for large permanent polarization of P(VDF-TrFE).

The lower degree of crystallization of as-cast film than the annealed samples makes it difficult to induce the permanent polarization (see Table I). The crystallinity of the as-cast film is approximately two-thirds of that of the annealed samples. The GIXD patterns from the annealed samples all display the similar preferred orientation near meridian. Both improved crystallinity upon annealing and preferred orientation of the c axis parallel to the substrate provide high remnant polarization, as shown in Figs. 1(b) and 1(c).

The sample heat treated above T_m exhibits the different diffraction pattern from the ones observed previously. The preferred orientation of the $\{110\}$, $\{200\}$ reflections is apparent near equator, indicating that the polymer crystals rotate 90° around the incident beam. The altered orientation results in the preferred alignment of the molecular chain axis c preferentially perpendicular to the substrate surface with both a and b axes parallel to the substrate. The rotation of crystals was observed in all the samples treated above T_m , irrespective of the cooling pathways (samples 6–8). The polar b axis, parallel to the substrate in this situation, rarely responds to the external electric field, giving rise to nearly zero net polarization as shown in Fig. 1(d).

GIRAS provides spectroscopic evidence of the crystal orientation modification during heat treatment. Figure 2(d) shows GIRAS of approximately 75 nm thick samples pre-

TABLE I. Ferroelectric properties and crystallinity for P(VDF-TrFE) films annealed at various temperatures.

Temperature (°C) /thickness (nm)	25/250	120/250	130/250	140/250	150/250	160/250	135/110	135/70
Remnant polarization ^a [P_r ($\mu\text{C}/\text{cm}^2$)]	1.2	7.75	8.35	8.73	0.55–1	0.55–1	11	8.33
Coercive voltage [V_c (V)]	N/A	10.9	10.7	11.22	N/A	N/A	7.27	4.95
Coercive field [E_c (MV/m)]	N/A	43.56	42.96	44.88	N/A	N/A	66.09	70.71
Crystallinity ^b (%)	45.89	59.48	63.22	63.77	60.5			

^aThe mean value from three different samples.

^bCalculated by the construction of crystallinity from the discrimination between the amorphous hump and the crystalline regions in GIXD curves.

pared with different conditions: one as cast, another annealed at 120 °C for 3 h, and the other slowly cooled from the melt. The annealing significantly increased the intensity of the band (A_1 , $\mu\parallel\mathbf{b}$) at 1289 cm^{-1} whose vibrational transition moment is parallel to the b axis. In addition, we observed the decrease of intensity at 1402 cm^{-1} (B_1 , $\mu\parallel\mathbf{c}$) band. These results indicate that the c axis tends to orient parallel to the substrate surface. For the sample cooled slowly from the melt, the c axis becomes perpendicular to the electrode surface confirmed by a significant intensity increase of B_1 band.

Electron microscopes permit direct visualization of the crystalline P(VDF-TrFE) microstructure related to the molecular chain orientation. Edge-on crystalline microdomains closely packed with needlelike shape are obvious on the surface of the film spun coated and annealed at 130 °C for 2 h [Fig. 3(a)]. The average length and width of the crystals are approximately 300 and 50 nm, respectively. The measurement of the light retardation using a polarized optical microscope (POM) suggests that the long axis of the crystals is parallel to the molecular chain axis (c axis). A needlelike crystal is composed of multiple stacks of crystalline lamellae along the long axis direction. GIXD, SEM, and POM results allow us to draw the schematic of the molecular and microstructural organization of the crystals, as shown in Fig. 3(c).

The microstructure of the film which underwent the melting and recrystallization is shown in Fig. 3(b). The surface was relatively smooth without a distinctive crystalline

microstructure. The flat surface was attributed to the in-plane lamellar structure where the chain axis, c axis, is dominantly normal to the substrate as confirmed by GIXD [Fig. 2(c)]. The polar b axis aligned parallel to the substrate is ineffective for the electric field applied perpendicular to the substrate, leading to the null polarization [Fig. 3(d)]. The similar microstructural modification upon heat treatment occurred in thinner polymer films [the inset of Fig. 3(a)].

The molecular orientation of P(VDF-TrFE) thin film with the polar b axis of the crystals, which is responsible for ferroelectricity, preferentially normal to the electrode surface was completely transformed into one with the b axis and the chain axis, c axis, of the crystals parallel and perpendicular to the electrode surface, respectively, during melting and recrystallization, leading to the irreversible extinction of ferroelectric polarization. The modification of the crystal orientation which should be avoided for realizing a nonvolatile memory device of P(VDF-TrFE) may be caused by the preferred interfacial energy between the crystalline ab plane and the electrode.

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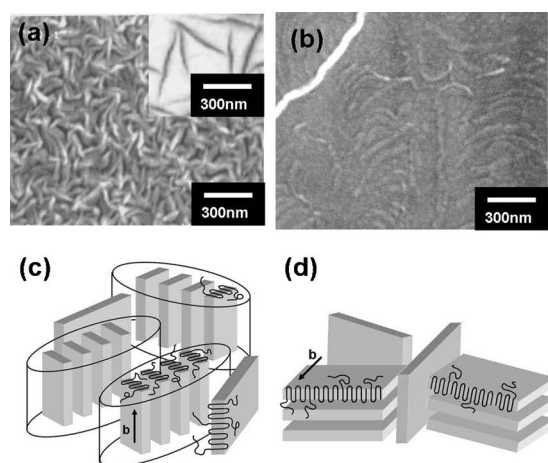


FIG. 3. (Color online) (a) SEM and TEM images (inset) of thin films annealed at 130 °C for 2 h. (b) A microstructure image of the melt-recrystallized film. (c) A schematic of microstructure shown in (a). (d) Schematic of microstructure shown in (b). The polar b axis is dominantly aligned parallel to the substrate.

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