

Crystalline structures and ferroelectric properties of ultrathin films of vinylidene fluoride and trifluoroethylene copolymer

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Abstract

Thin and ultrathin films of copolymer of 83% mole fraction vinylidene fluoride and 17% mole fraction trifluoroethylene were prepared using a spin-coating technique. Atomic force microscopy results showed that spun films formed tiny grains on the surface. A micro-thermal analyzer showed that tiny grains had a ferroelectric Curie transition at 128.8 °C and melted at 140.7 °C. The crystallinity of the film was measured to be ca. 40% by an X-ray diffraction for the film with thickness above 170 nm. Crystallinity decreased quickly with decreasing thickness. The crystallinity was at most 5% for the film with thickness below 75 nm. We found the ferroelectric polarization reversal effect strongly depended on the film thickness. Clear polarization reversal due to a switching of ferroelectric dipoles was observed for the film with thickness above 90 nm and broad ferroelectric reversal was obtained for the film with thickness below 90 nm. For the films with thickness above 100 nm, the remnant polarizations were almost constant and the coercive fields were significantly decreased with decreasing film thickness.

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1. Introduction

For vinylidene fluoride and trifluoroethylene (P(VDF-TrFE)) copolymers, large spontaneous polarization is cooperatively switched by an alternating external electric field greater than 100 MV/m. The switched spontaneous polarization is stabilized by van der Waals interaction between molecular chains. This is the reason for having a large coercive field in the P(VDF-TrFE) copolymer. Traditionally, to achieve a high electric field over 100 MV/m, a high voltage up to 10 kV must be applied to the sample film with a typical thickness of 50 to 100 μm. However, the recent development of thin film with thickness less than 100

nm enables us to use an applied voltage as low as 10 V to achieve 100 MV/m for the same switching effect. This development has opened many new applications such as organic ferroelectric memory devices for computers and related devices. Extensive studies of ferroelectric thin films of P(VDF-TrFE) have been reported. Most of these studies concentrated on their properties such as ferroelectricity, piezoelectricity and pyroelectricity, and the applications such as transducer and ultrasonic sensors.

To address those applications properly, fundamental characterization of the ferroelectric performance of the copolymer film with thickness below 100 nm is needed. Recently, there are reports on discontinuous changes in crystallization for P(VDF-TrFE) copolymer thin film for thickness below 100 nm [1,2], which was correlated to the ferroelectric properties such as polarization reversal [3,4], and polarization switching time [4,5]. Ferroelectric films made by Langmuir method were also investigated [6,7].

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Table 1
Typical thicknesses of films as a function of solution concentration and spin speed

Solution concentration (%)	0.5		1.0		2.0		4.0		8.0		16.0
Spin speed	500	1000	500	1000	500	1000	500	1000	500	500	500
Thickness (nm)	35	20	76	61	180	90	540	400	1900	30000	

Employing a conductive polymer as the bottom electrode, large improvement of polarization switching time is achieved with low voltage of 5.2 V for sub-100-nm-thickness P(VDF-TrFE) film [8]. Crystallite structures and ferroelectricity of vinylidene oligomers have also been studied [9,10]. Layer-thinning effects on ferroelectricity and the ferroelectric-to-paraelectric phase transition of P(VDF-TrFE) layers were investigated [11]. Effects of thickness in the range of 0.03–1 μm on ferroelectricity in P(VDF-TrFE) were investigated [12]. Substrate effect in local poling of ultrathin P(VDF-TrFE) films was investigated [13].

In this paper, we report results from a detailed study of crystalline structures and ferroelectric properties for thin and ultrathin films of the P(VDF-TrFE) copolymer with 83 mol fraction VDF and 17 mol fraction TrFE. We investigated the thickness dependence of surface morphology, thermal properties, crystallinity, electrical and ferroelectric properties (coercive field and remnant polarization) of the films. The thickness of the films covered in this study ranged from 100 μm to 20 nm, commonly referred to as ultrathin films.

2. Experimental

P(VDF-TrFE) copolymer (83:17, molar ratio) was used to prepare thin (100 nm or thicker) and ultrathin (100 nm and thinner) copolymer films. The films were prepared on an aluminum electrode evaporated glass substrate using a spin-coating technique. The film thickness was controlled by changing the concentration of P(VDF-TrFE) in a solution as well as the spin speed, and was in the range of 20 nm to 400 nm. The concentration of P(VDF-TrFE) in methyl ethyl ketone (MEK) or dimethyl formamide (DMF) was 0.5%, 1.0%, 2.0%, 4.0%, 8.0% and 16.0% by mass fraction. Spin speeds were 500 and 1000 revolution per minute. A counter aluminum electrode was evaporated on the film after spin coating and then the sample film was annealed at 120 $^{\circ}\text{C}$ for 4 h.

The surface morphology of thin and ultrathin films was measured using a Digital Instruments atomic force microscope (AFM) in a contact mode. The cross-sectional image of film was measured to evaluate thicknesses of thin and ultrathin films.²

² Certain instruments and materials identified in this paper are to adequately specify experimental details. In no case does it imply endorsement by NIST or that those are necessarily the best for the purposes specified.

Thermal analysis of tiny spots on the films was conducted using a TA Instruments micro-thermal analyzer using a heating rate of 10 $^{\circ}\text{C}/\text{s}$. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 7 and a TA Instruments DSC 2920 differential scanning calorimeters at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. The systems were calibrated using the melting temperature of indium metal. X-ray diffraction pattern of films was recorded using a Mac Science X-ray diffractometer with nickel filtered $\text{Cu K}\alpha$ radiation. Infrared spectra of films were recorded with a reflection mode using a Perkin Elmer model Spectrum GX FT-IR spectrometer equipped with an optical microscope.

Capacitance was recorded on a HP model 4194A Impedance Analyzer. The poling current of the films was monitored during the application of sinusoidal voltage using a current amplifier. The remnant polarization (P_r) and the coercive field (E_c) were determined from the polarization charge by integrating the poling current. The combined standard uncertainties on the electrical measurements were less than 10%.

3. Results and discussion

Thin and ultrathin films were spin-coated on an aluminum electrode evaporated glass substrate from MEK or DMF solution with different concentrations of the P(VDF-TrFE) copolymer. The edge part of the film was peeled off using a blazer knife to measure the thickness of films. The AFM cross-sectional image was used to determine the thickness of all films. Typical thicknesses of films as a function of solution concentration and spin speed are listed in Table 1. Fig. 1 shows AFM topographic image of spun films prepared from 2% mass fraction copolymer solution. Tiny grains were found on the surface of the films. Grain size prepared from MEK solution (Fig. 1(b)) is smaller than that from DMF solution (Fig. 1(a)). The size of these grains increased with increasing solution concentration.

Fig. 2 shows thermograms of the flat surface and the grain areas measured using a micro-thermal analyzer. Sample film was prepared from DMF solution. A micro-thermal analyzer is a useful tool for investigating thermal properties of micro-size areas of surface. A thermocouple AFM probe tip sensitively detected the thermal change in the micron-size areas of the surface. The thermogram of grain part gives the distinct two inflection points (peak) at 128.8 $^{\circ}\text{C}$ and 140.7 $^{\circ}\text{C}$ which we attributed to Curie and melting transitions, respectively. DSC thermograms of the

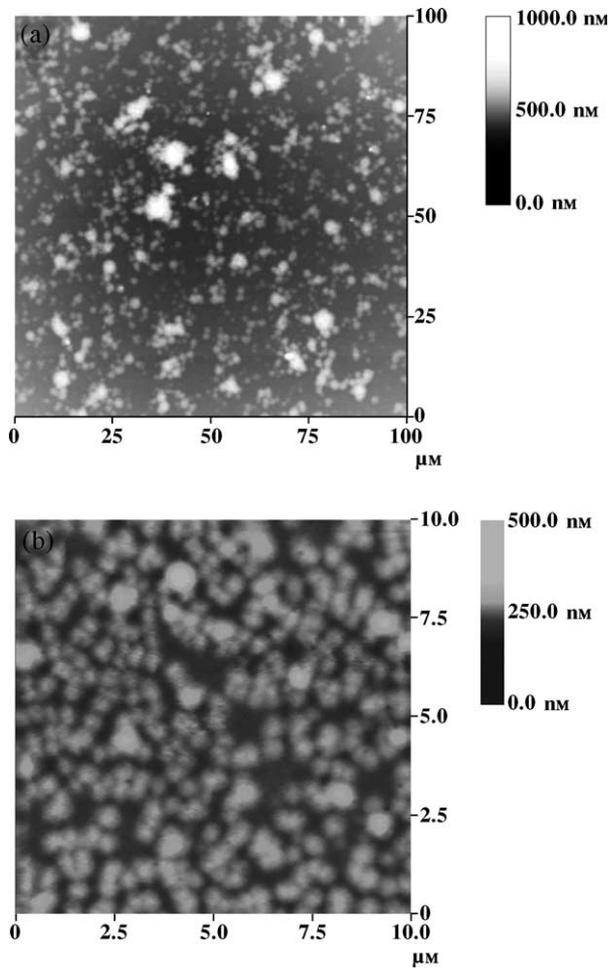


Fig. 1. AFM images for the films prepared from DMF (a) and MEK (b) solutions.

same powder sample of copolymer gave a Curie transition at 130.8 °C and a melting transition at 142.8 °C. On the other hand, there is no observable change in thermogram of the flat part measured by the micro-thermal analysis. These results showed that the grains on the film were ferroelectric crystallites and the flat part was almost amorphous.

Fig. 3 shows X-ray diffraction patterns measured from the films of thicknesses of 38 nm, 75 nm and 170 nm (a) and those of 0.52 μm, 1.3 μm, 25 μm and 100 μm (b). Typical diffraction peaks due to reflections from (110) (200) of the β crystal are observed at $2\theta=20.1^\circ$. Diffracted peaks are separated with Gaussian peaks as shown in Fig. 3(c) and (d). The crystallinity is evaluated by the ratio of peak area at $2\theta=20.1^\circ$ to total area for the film of different thicknesses in the range from 38 nm to 100 μm. The crystallite size of β crystal was estimated from the half-width at $2\theta=20.1^\circ$, using an Scherrer relation. Crystallinity and crystallite size are plotted as a function of film thickness in Fig. 4. The film with thickness above 170 nm has an almost constant crystallinity of 40%. On the other hand, films with thickness below 170 nm have decreased crystallinity. The films of 38 nm and 75 nm have crystallinity less than 5%. However, the

crystallite sizes are relatively constant. It varies from 12 nm to 15 nm in thickness while the crystallinity is constant. However, even for the 38 nm film the crystallite size is 8.8 nm. From these results, we believe the size of the crystallites is the key limitation to the formation of a highly crystalline ferroelectric ultrathin film.

The changes in crystallinity with changes in film thickness were also confirmed by a microscopic FT-IR with reflection mode. Fig. 5 shows the FT-IR spectra of films with different thicknesses in the range from 35 nm to 1.9 μm. It was found that peak at 1075 cm^{-1} due to the crystallite [14] appeared for the film with thickness above 180 nm and its intensity increases with increasing film thickness and leveled out.

The reciprocal value of capacitance measured at 1 kHz has linear relationship with a function of film thickness. The slope gives the relative permittivity (dielectric constant) of P(VDF-TrFE) copolymer thin sample. A relative permittivity, ϵ , of 10.7 was measured from the slope.

It is well known that ferroelectric dipoles of P(VDF-TrFE) copolymer are cooperatively switched when a sinus-

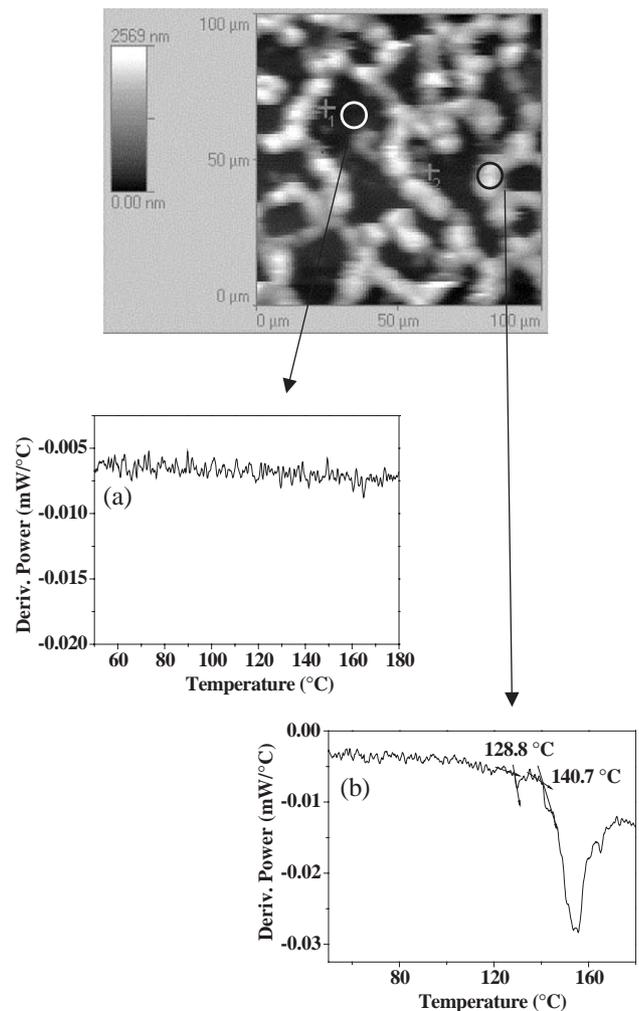


Fig. 2. Thermograms of film surface using a micro-thermal analyzer. (a) Flat area and (b) grain part.

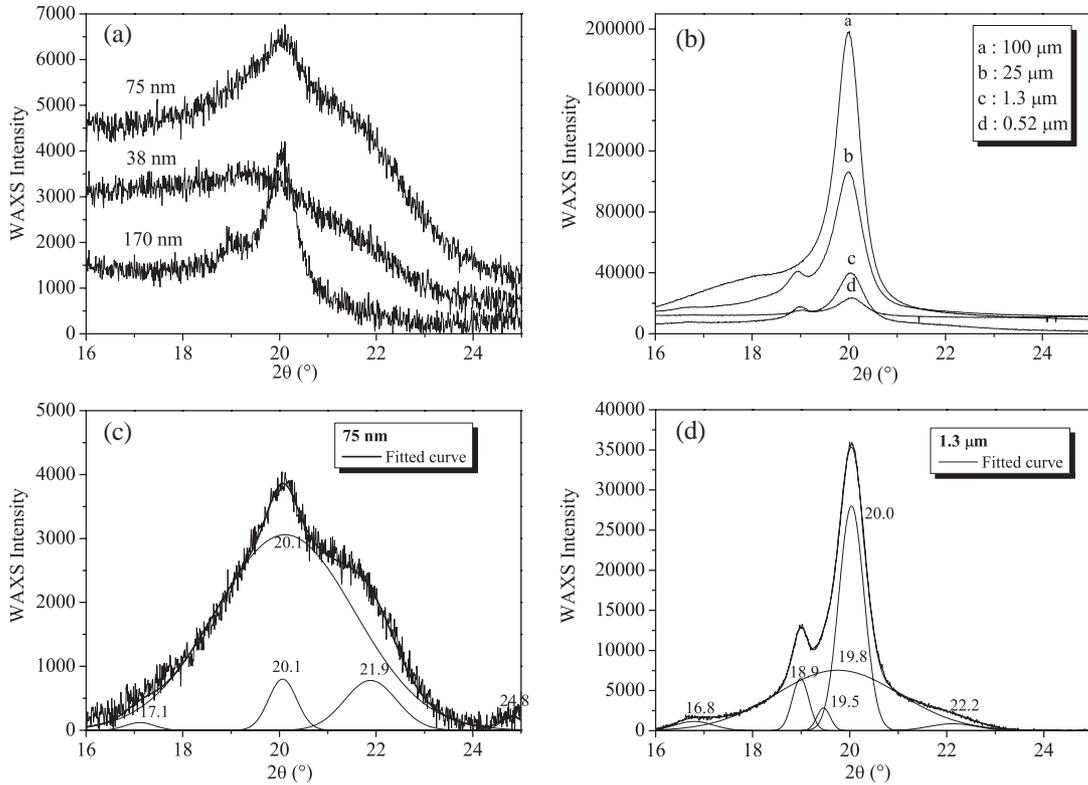


Fig. 3. X-ray diffraction patterns for films with thickness of 38 nm, 75 nm and 170 nm (a) and those of 0.52 μm, 1.3 μm, 25 μm and 100 μm (b). Examples of curve fitting using Gaussian peaks for diffraction patterns of film with thickness of 75 nm (c) and those of 1.3 μm (d).

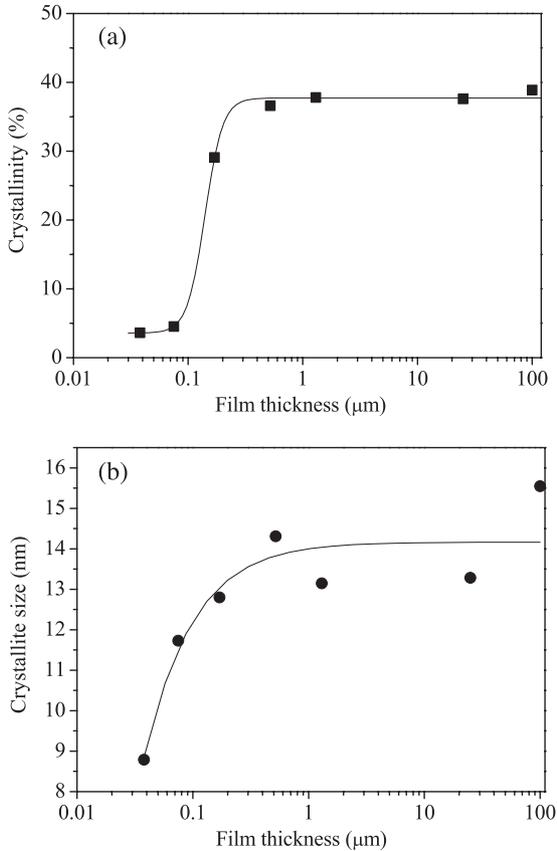


Fig. 4. Plots of crystallinity (a) and crystallite size (b) as function of film thickness.

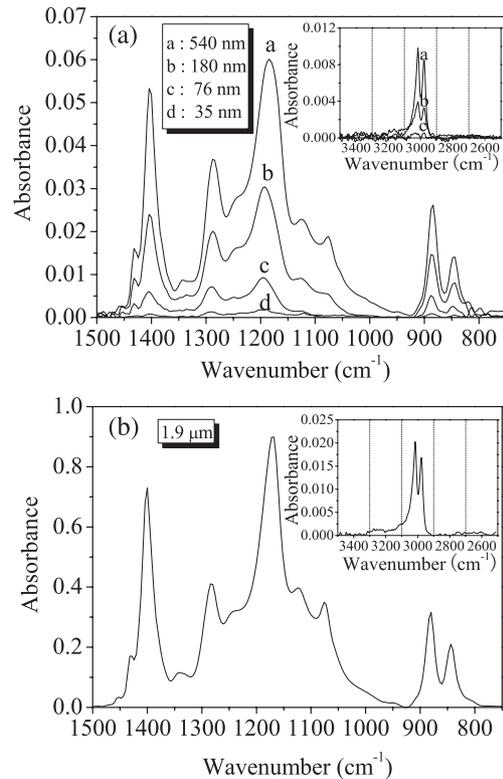


Fig. 5. FT-IR spectra for films with thickness of 35 nm, 76 nm, 180 nm, 540 nm and 1.9 μm using FT-IR equipped with a microscope with reflection mode.

oidal external electric field is applied. Fig. 6 shows the current flow when the sinusoidal electric field of different frequencies in the range of 50 mHz to 1000 mHz is applied to thin film of 61 nm and 170 nm thick. The current flow on the external circuit is the summation of the current due to polarization, capacitance and conductivity [15]

$$J = J_D + J_\rho = \frac{dP}{dt} + \varepsilon\varepsilon_0 \frac{dE}{dt} + \frac{E}{\rho}$$

where J is the poling current, J_D is the displacement current, J_ρ is the conduction current, P is polarization, ε is the relative permittivity, ε_0 is the permittivity of vacuum, and E is the applied electric field. After subtraction of capacitance and resistance terms from the observed current flow, the electric displacement due to polarization was determined. The polarization charge vs. applied electric field is shown for thin films with 61 nm and 170 nm thicknesses in Fig. 7. The intercept on P -axis gives a remnant polarization P_r and that on E -axis a coercive field E_c . It is found that P_r and E_c values are dependent on the frequency of the sinusoidal electric field. The P_r and E_c values normalized by those at 50 mHz are plotted as a function of frequency of sinusoidal electric field in Fig. 8. E_c values increase with increasing frequency for the sample with thickness above 100 nm, and decreases with increasing frequency for the sample with

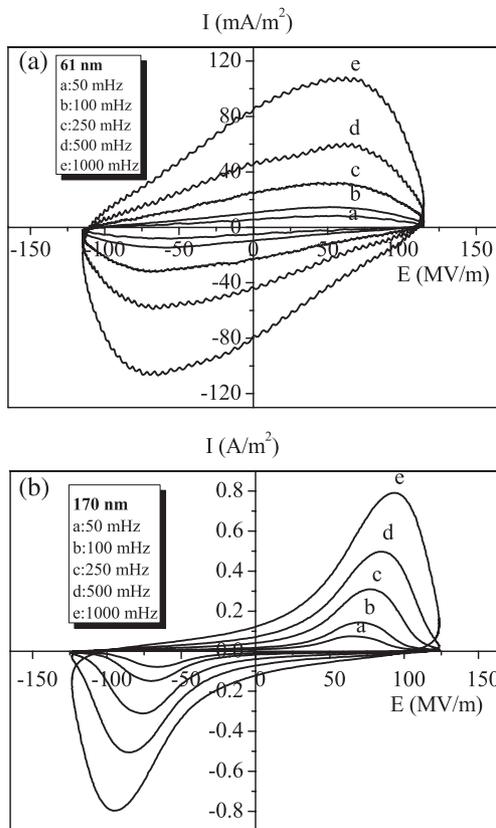


Fig. 6. Current flow when applying high electric field with different cycling frequencies for the film with thickness of 61 nm (a) and those of 170 nm (b).

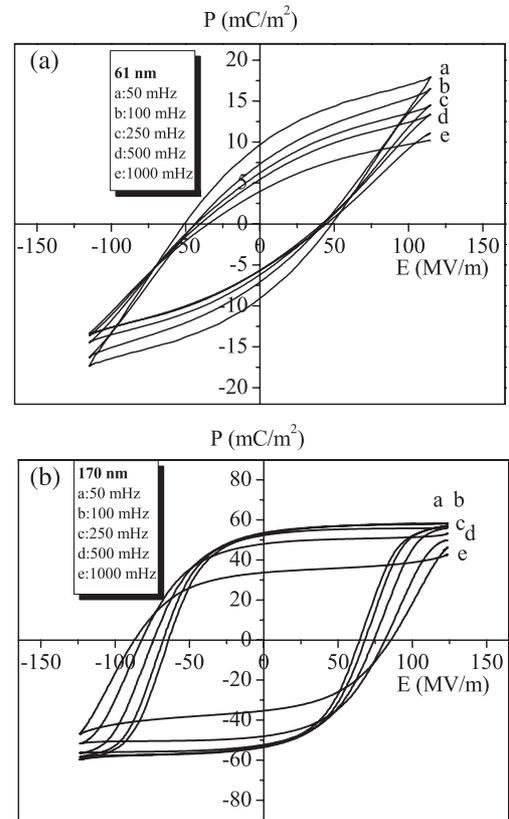


Fig. 7. Polarization charge profiles obtained from the time integration of current flow in Fig. 6.

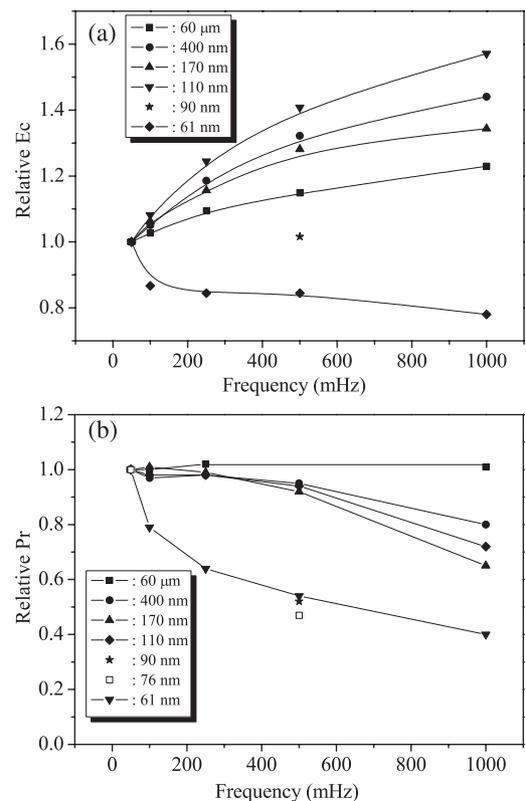


Fig. 8. Plots of relative P_r and E_c values, which were normalized by those at 50 mHz, vs. cycling frequency.

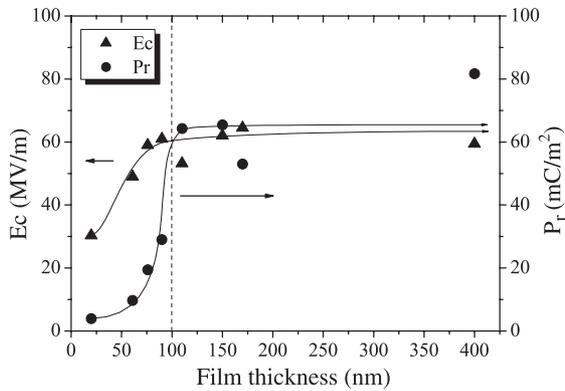


Fig. 9. Plots of P_r and E_c values vs. film thickness.

thickness below 100 nm. No dependence of P_r values on frequency was observed for the sample with thickness 60 μm , whereas P_r values decrease with increasing frequency for thin films. For the sample with thickness below 100 nm, depression of E_c follows the depression of P_r with increasing frequency. These results imply that ferroelectric domains in the sample with thickness below 100 nm have difficulty for polarization switching at higher frequency. Namely, the confined space within 100 nm thickness restricts the polarization switching at higher frequencies of the electric field (the finite size effect) and/or containing interaction between films and aluminum electrode substrate was distinct in a film with thickness below 100 nm.

The current flow and polarization charge were measured as a function of the thickness of films. The maximum applied electric field was 125 MV/m. For the film with thickness above 90 nm, distinct polarization reversals were measured in the poling current flow, whereas for the film with thickness below 76 nm, only broad polarization reversals were measured. P_r and E_c values obtained are plotted as a function of film thickness in Fig. 9. Almost constant P_r and E_c values are measured for the films with thickness above 100 nm, whereas they significantly decrease with decreasing film thickness in the range below 100 nm. The decrease of P_r and E_c values for the sample with thickness below 100 nm is ascribed to their lower crystallinity and the restriction of polarization switching in the confined space within the thickness below 100 nm. The critical thickness of P_r and E_c was 100 nm and that of crystallization was 170 to 180 nm. These critical thicknesses are in agreement with those previously reported [5]. Earlier study showed that the increase of E_c was followed by decreasing film thickness [3,16]. However, in the present case, the decrease of E_c occurred when the film thickness was below 100 nm. The discrepancy should be clarified in the future. However, for the present time, it is clear that good quality films for application should be able to form at thickness level of 100 nm. Less than 100 nm the formation of film was limited by the ability of forming of crystallites and therefore reduces the crystallinity of the films.

4. Conclusion

The surface morphology, crystallization and ferroelectric properties of ultrathin films of P(VDF-TrFE) copolymer have been studied. A micro-thermal analysis showed that tiny grains had a ferroelectric Curie transition at 128.8 $^{\circ}\text{C}$ and melting of crystallite at 140.7 $^{\circ}\text{C}$. A large depression of crystallinity and that of ferroelectric properties were observed in the thickness region below 180 nm and 100 nm, respectively. These critical phenomena were ascribed to the large restriction for crystallization due to depression of molecular mobility in the confined space of ultrathin film with thickness below 180 nm in addition of interaction between films and aluminum electrode occurs for the sample with thickness less than 100 nm. The observation placed an application limit on the thin film at 100 nm unless there is a significant improvement in the processing of this class of films.

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