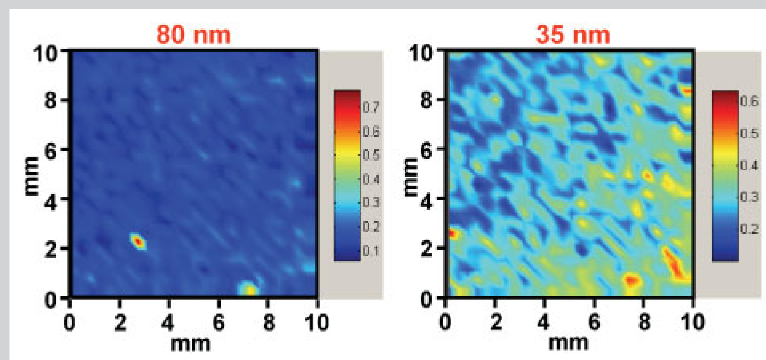
Summary: Highly crystalline ferroelectric polymer films [vinyidene fluoride and trifluoroethylene, β-P(VDF-TrFE), 260–15 nm thick] were characterized with FTIR reflectance-transmission microspectroscopy (FTIR-RTM) mapping technique (400 µm × 400 µm spatial resolution). The amorphous and crystalline fractions were identified locally. FTIR-RTM maps (1 cm^2 area) provided a unique in-depth view of the ultrathin films. Lower film thickness suppressed growth of the crystalline phase. Increased content of amorphous phase lead to non-uniform films with degraded ferroelectric behavior.



FTIR-RTM maps of the distribution of the amorphous phase in the 80 and 35 nm films.

Micro FTIR Mapping of Nanometer Ferroelectric Polymer Films

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Introduction

Ferroelectric polymers are considered one of the most important electronic polymer groups that have many applications such as transducers, ultrasonic sensors, memory, and storage devices, etc. Electronic device applications have been developed based on conventional poly(vinyidene fluoride) (PVDF) polymer films [(10–100) µm thick] that required high voltage (up to 1 kV) to operate.[1] Soluble poly(vinyidene fluoride and trifluoroethylene) P(VDF-TrFE) copolymers that have been reported later[2,3] were processed into submicron thin films for physical studies.[4] Recently, ultrathin films at nanometer thickness were developed for reexamining the fundamental nature of ferroelectricity, such as intrinsic ferroelectric coercive field.[5–8] When the thickness of the films was reduced by over 1 000 times, the applied voltage was reduced to the electronic logical level.[9] Therefore, ultrathin films open the door to a wide range of modern electronic applications including polymer computing.

Although the ferroelectric properties of the ultrathin films had received great attention, little effort was made to study the many basic characteristics of these films, which are needed to properly interpret their electrical properties.

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Infrared spectroscopy (IR) is a fundamental measurement made to identify and characterize a polymer film. For characterizing ultrathin film deposited on a non-transparent reflective substrate, we have developed a micro Fourier transform infrared (FTIR) method to measure the IR spectrum. Applying FTIR microspectroscopy in reflectance mode to a reflective substrate covered with a thin polymer film results in reflection-transmission spectra (FTIR-RTM).[10] By scanning the film we build up an IR image of selected IR characteristics of the film. Such an FTIR map shows the microstructure of a polymer film, its thickness is only at the nanometer scale, but over area greater than 1 cm × 1 cm. This unique spectroscopic information can be critical for thin film physics and for future applications of these ultrathin films.

In this paper, we report the results of the first micro FTIR mapping of ferroelectric β-P(VDF-TrFE) polymer ultrathin films. We analyzed these infrared spectra for amorphous and crystalline phases within the film and their spatial distributions. By decreasing the thickness of the film, we found that the limit for uses in electronic is about 100 nm, due to the inhibition of the crystalline phase at thinner films.

Experimental Part

Films Preparation

Commercial copolymer of 83 mol-% vinyidene fluoride and 17 mol-% trifluoroethylene (VDF-TrFE) (copolymer) was used in this study. Nanometer scale copolymer thin films on Al-coated glass substrate were prepared by the spin-coating technique.[11] The copolymer was completely dissolved into *N*,*N*-dimethylformamide (DMF) to form dilute spin-coating solution. In order to insure that the polymer was indeed fully dissolved, we allowed the solutions to age for more than a week at room temperature before use. The concentrations of the copolymer in the solutions were 0.53, 1.1, 2.4, 4.2, and 7.9% by mass. The spin-coating was done at a constant speed of 1 000 rpm and ambient temperature. The surface of the glass substrate was pre-coated with a layer of metallic aluminum by the thermal evaporation method.[11] The thickness of the metallic aluminum and the copolymer films was measured with atomic force microscope (Dimension 3100 Nanoscope IIIa, Veeco Instruments, Inc., Woodbury, NY, USA). The thickness of the metallic aluminum layer was about 150 nm. The thickness of the copolymer films that were prepared under the same experimental conditions varied linearly with the concentration of the solutions. Therefore, unless specified, the thicknesses of the resulting films were 15, 35, 80, 140, and 260 nm. All films were studied as-prepared without further processing.

FTIR Analyses

Drops of DMF solution of VDF-TrFE were placed on a KBr window and the film formed after 7.5 h was measured in a Nicolet Nexus 670™ FTIR spectrophotometer (Nicolet Instrument Corporation, Madison, WI, USA) continuously purged with dry air. The IR spectrum was collected between 4 000 and 400 cm^{-1} at a resolution of 2 cm^{-1} with 1 000 co-added scans.

Poly(vinyidene fluoride) fine powder (0.33 mg) was thoroughly mixed with 400 mg of spectroscopic grade KBr (dried) and pressed into a pellet (13 mm diameter, 1 mm thick). IR spectrum was collected between 4 000 and 400 cm^{-1} at a resolution of 2 cm^{-1} with 184 co-added scans using the same FTIR spectrophotometer described above.

FTIR-RTM Measurements

The FTIR-RTM measurements were done using a Nicolet Magna-IR 550 FTIR spectrophotometer interfaced with a Nic-Plan IR microscope (Thermo Nicolet Inc. Madison, WI, USA). The microscope is equipped with a video camera, a liquid nitrogen cooled-mercury cadmium telluride (MCT/A) detector, and a computer-controlled mapping stage (Spectra-Tech, Inc., Shelton, CT, USA), programmable in the x and y directions. Individual spectra that were used for peak separation were measured from representative spots on the films with a high number of scans in order to increase the signal-to-noise ratio. Point-by-point spectral mapping of the films was carried out in a grid pattern with the computer-controlled microscope stage and Omnic Atlus software (Thermo Nicolet Inc. Madison, WI, USA) with spatial resolution of 400 μm × 400 μm. Each spectrum was collected between 4 000 and 650 cm^{-1} at a spectral resolution of 8 cm^{-1}. The FTIR-RTM spectra were ratioed against a control Al substrate and converted to absorbance without any mathematical correction.[10] The map spectra were collected with 128–192 scans for each spectrum. Individual spectra were collected from representative spots of the various films with high number of scans (1 000–10 000 scans for the thinnest films). For each individually collected spectrum, a detailed peak fitting analysis was performed with PeakFit (Jandel Corporation, San Rafael, CA, USA) to separate the peaks by their areas, using linear baseline and Gauss peak area function. The separated peaks that relate to the amorphous and to the crystalline phases were identified and their areas were used to compute the ratios between the amorphous and the crystalline phases. The analyses of peaks in large array of spectra (676 spectra in each map) was done simultaneously on all the map spectra, using the recently revised[10] ISys software (Spectra Dimensions, Olney, MD, USA).

To characterize the electrical switching behavior of the film, we measured the poling current of films during the application of a sinusoidal voltage. Remnant polarization (P_r) versus coercive field (E_c) is calculated by integration of the poling currents.[11] Films with thickness of 20 and 100 nm were used for these measurements.

Results and Discussion

Figure 1 shows a comparison between an FTIR spectrum of P(VDF-TrFE) copolymer measured with the FTIR-RTM method [(b) obtained from an Al-coated film], and spectra acquired with traditional transmission FTIR spectroscopy

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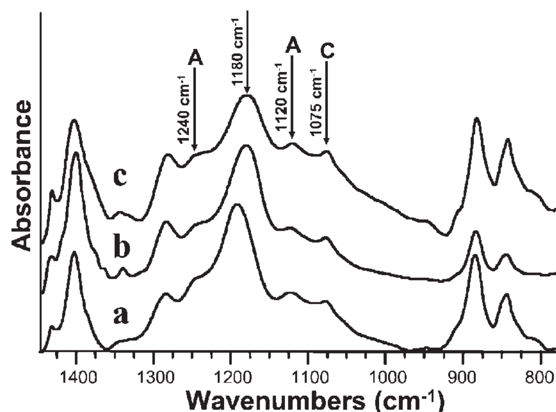

Figure 1. FTIR spectra of P(VDF-TrFE) copolymer. (a) PVDF powder embedded in KBr (FTIR spectrophotometer, transmission, spectral resolution = 2 cm^{-1}, 184 scans); (b) 260 nm film spin-coated on Al (FTIR-RTM, spectral resolution = 8 cm^{-1}, 1 000 scans); and (c) film deposited on KBr window (FTIR spectrophotometer, transmission, spectral resolution = 2 cm^{-1}, 1 000 scans).

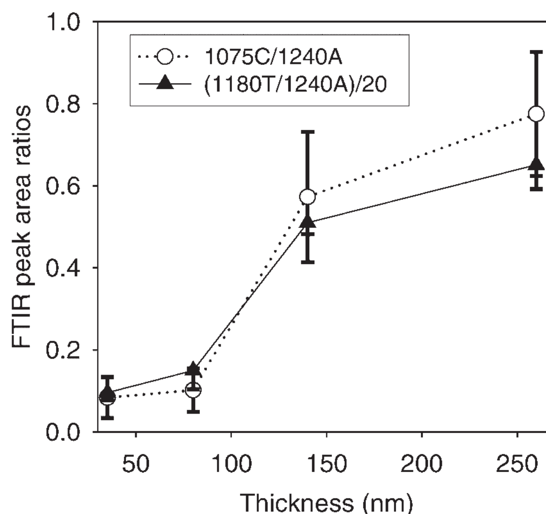

Figure 2. The averages and SDs of ratios between FTIR peak areas relate to crystalline and amorphous P(VDF-TrFE) phases, obtained from the 35, 80, 140, and 260 nm films are shown as a function of film thickness; $n = 6$ for the 80 nm film, $n = 4$ for the rest of the films. Blue circles: crystalline peak (1 075 cm^{-1})/ amorphous peak (1 240 cm^{-1}). Red triangles: (1 180 cm^{-1})/ (1 240 cm^{-1}) peaks. Lines drawn to aid the eye of the reader. Error bars represent the experimental uncertainty at each thickness.

[(a) obtained from a KBr pellet containing PVDF powder and (c) obtained from a KBr window coated with P(VDF-TrFE) film]. The FTIR-RTM spectrum that was obtained from a 400 μm × 400 μm sample area correlated well with both transmission spectra obtained from a large area of a KBr window coated film and from the PVDF powder embedded in KBr pellet. As can be seen, the three spectra acquired with three different methods are almost identical and the peak locations are similar and match published results obtained from a PVDF film,[12] although the relative intensities are somewhat different. The slight intensity difference between different experimental methods does not affect the identification of polymer phases. The amorphous (1 240 cm^{-1} peak) and the crystalline (1 075 cm^{-1} peak) phases identified in the traditional FTIR spectra as well as the FTIR-RTM spectra agreed with earlier work.[12]

Figure 2 shows the crystallinity of P(VDF-TrFE) copolymer films as a function of the thickness of the copolymer film. We used the small but well-defined peak at 1 075 cm^{-1} (separated with PeakFit from the individual spectra that were collected with high number of scans) to identify the crystalline phase of PVDF. The ratio between the 1 075 cm^{-1} IR peak attributed to the crystalline phase and the 1 240 cm^{-1} IR peak attributed to the amorphous phase was used in Figure 2 for normalizing variations in the internal thickness of each film. Figure 2 revealed that the crystallinity of the copolymer films decreased with decreasing thickness of the various films. The change of dielectric properties around 100 nm has been observed in earlier studies with SEM and X-ray diffraction.[13,14] The exact critical thickness, however, was dependent on solvent and processing conditions. Figure 2 demonstrated that the observed changes in dielectric properties and ferroelectric behaviors originated from the change of crystallinity in the film.

A small peak, such as the crystalline peak at 1 075 cm^{-1}, is too weak for using in analyses of spectra acquired by automatic FTIR-RTM mapping of nanometer films. Note also that the map spectra were collected with a smaller number of scans (128 or 192 scans per spectrum) than the individual spectra that were used for Figure 2 (up to 10 000 scans per spectrum). Therefore, for quantitative evaluation of the crystalline phase in the copolymer film maps, we chose the larger peak at 1 180 cm^{-1} (CF_2 antisymmetric stretching mode).[15] As can be seen in Figure 2, the ratios between the areas of the 1 180 and 1 240 cm^{-1} and that of the 1 075 and 1 240 cm^{-1} followed the same trend and were different from each other by a constant factor of 20. Based on the qualitative correlation between the crystalline to amorphous peaks (1 075–1 240 cm^{-1}) and the (1 180–1 240 cm^{-1}) peaks, the ratios between the 1 240 cm^{-1} amorphous peak and the 1 180 cm^{-1} peak were used as a relative measure of the amorphous to crystalline phases present in the whole films. Hence, the 1 180 cm^{-1} peak represents the crystalline phase in the processed FTIR-RTM maps.

Figure 3 shows micro FTIR mapped images of the distribution of the amorphous phase in the 35 and 80 nm P(VDF-TrFE) copolymer films. The digital images contain 676 pixels each of numerical data, which are the ratios

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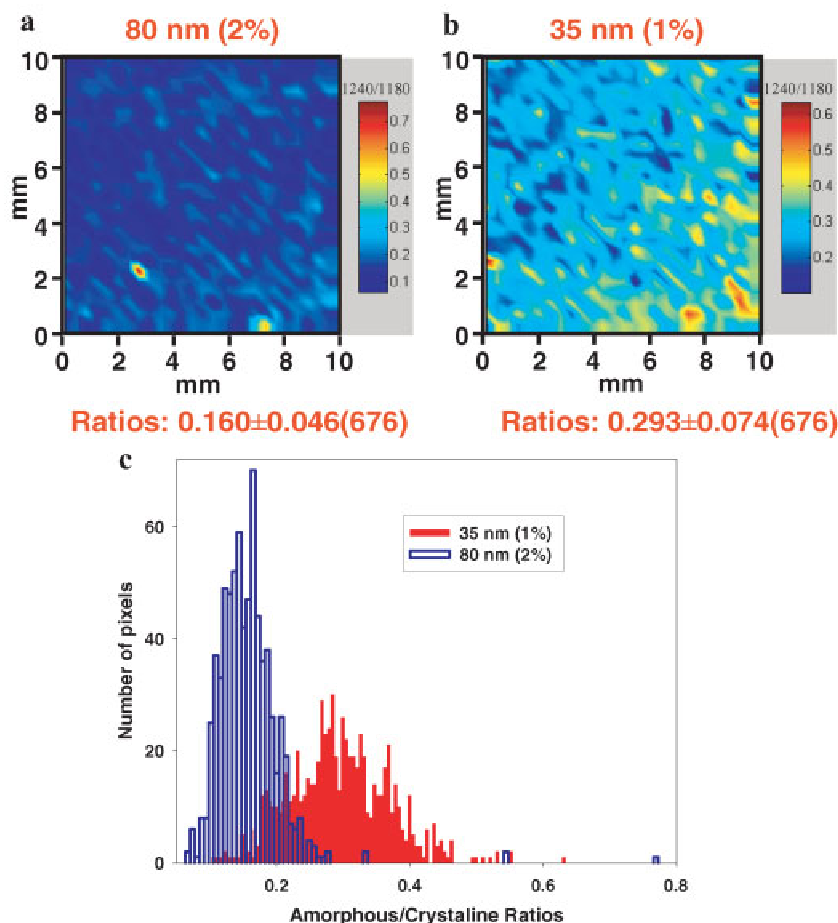

Figure 3. FTIR-RTM maps of the distribution of the amorphous phase in the 80 and 35 nm films [(a) and (b) respectively]. (c) The histograms of the peak ratios: (1 240/1 180) cm^{-1} in the FTIR images shown in (a) and (b).

between the integrated areas under the same selected 1 240 and 1 180 cm^{-1} peaks of each individual FTIR-RTM spectrum at the corresponding location of the films. The ratios, which are independent of thickness variations of the film, represent the relative amount of the amorphous phase in the film. The micro FTIR mapping images are arrays of spectra obtained from nanometer films over the physical area of 1 cm $\times$ 1 cm. The color scale indicates the relative amount of the amorphous phase in that location on the film. It can be seen from the images that the 80 nm film is more uniform than the 35 nm film (mainly blue colors vs. colors from the entire color scale) and that the 35 nm film has much more amorphous area than that of the 80 nm. The relative amount of the amorphous phase in the 35 nm film is almost twice than that in the 80 nm film (0.293 ± 0.074 vs. 0.160 ± 0.046, $n = 676$). One standard deviation (SD) represents the experimental standard uncertainty of the spectra collection and processing. The %SD is about the same, but the histograms in Figure 3(c) support the visual observation that the 80 nm film is more uniform than the 35 nm film (a narrower distribution, even when all the pixels are included).

We can conclude from both visual examination of the images and the statistical data of the variation of the pixels that 80 nm films could have the uniformity to be considered for building microelectronic applications with near millimeter device size. This is the first time that the bulk macrostructure of nanometer thick P(VDF-TrFE) copolymer films has been characterized with micro FTIR mapping over 1 cm $\times$ 1 cm areas at once. In contrast to many common imaging methods, such as atomic force microscopy that often only provide the information of small isolated regions (up to 2 μm $\times$ 2 μm in Kimura et al., 2003[16] for example), micro FTIR images provide a unique insight into the internal microstructure of a P(VDF-TrFE) polymer film large areas (1 cm $\times$ 1 cm).

Figure 4 shows the comparison of switching behaviors of 100 and 20 nm P(VDF-TrFE) polymer films.[11] Clear polarization reversal due to a switching of ferroelectric dipoles was observed for the film with thickness above

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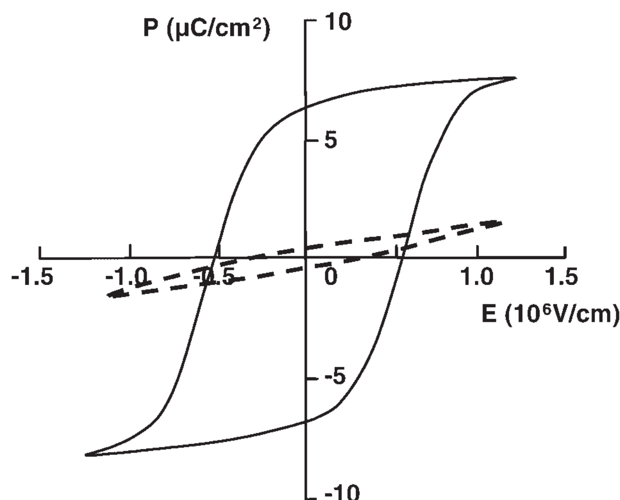

Figure 4. Clear switching behaviors can be observed for 100 nm P(VDF-TrFE) copolymers film (solid line), not in 20 nm films (dashed line).

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. This is critical for switching and memory applications.

In summary, we presented the results of FTIR-RTM studies of ultrathin, highly crystalline ferroelectric polymer nanometer films from 200 nm down to 35 nm. The relative contents of amorphous and crystalline phases in the ultrathin films were estimated. By mapping a large area at a relevant scale for electronic applications with FTIR-RTM, and interrelating the local morphology, we obtained a unique polymer property image for an ultra thin polymeric film. In this case, the distributions of morphology of spin-coated P(VDF-TrFE) copolymers ultrathin films were clearly displayed in the form of visual color images on a practical scale. The degree of uniformity is displayed in pseudo-color images.

Conclusion

The crystalline phase content decreased and the amorphous phase content increased as the film thickness decreased as shown earlier by SEM and X-ray diffraction techniques.[13,14] The 80 nm film was more uniform than the 35 nm film and the relative amount of the amorphous phase in the 35 nm film was almost twice than that in the 80 nm film. The observed changes in dielectric properties and ferroelectric behaviors originated from the change of crystallinity in the films. It can be concluded from the visual examination of the images and the statistical data of the variation of the pixels that 80 nm films could have the suitable uniformity to be considered for building microelectronic applications with near millimeter device size. Combination of the electrical data and the FTIR-RTM mapping information can contribute to a better evaluation of the properties of very thin films for use in modern applications. This unique method of displaying physical properties of a thin polymer film is crucial to future applications of films at the level of nanometer thickness.

Disclaimer

Certain commercial materials and equipment are identified for adequate definition of the experimental procedures. In no instance does such identification imply recommendation or endorsement by NIST that the material or the equipment is necessarily the best available for the purpose.

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[1] T. T. Wang, J. M. Herbert, A. M. Glass, ''*The Applications of Ferroelectric Polymers*'', Chapman & Hall, New York 1988.
[2] T. Furukawa, M. Date, E. Fukada, *Jpn. J. Appl. Phys.* **1980**, *19*, L109.
[3] M. Uchidoi, T. Iwamoto, K. Iwama, M. Tamura, T. Yamada, T. Ueda, T. Kitayama, *26th Meeting, Jpn. Soc. Appl. Phys. Related Sci., Preprint.* **1979**, 326.
[4] K. Kimura, H. Ohigashi, *Appl. Phys. Lett.* **1983**, *43*, 834.
[5] S. Ducharme, V. M. Fridkin, A. Bune, S. P. Palto, L. M. Blinov, N. N. Petukhova, S. G. Yudin, *Phys. Rev. Lett.* **2000**, *84*, 175.
[6] A. M. Bratkovsky, A. P. Levanyuk, *Phys. Rev. Lett.* **2001**, *87*, 19701.
[7] R. L. Moreira, *Phys. Rev. Lett.* **2002**, *88*, 179701.
[8] S. Ducharme, V. M. Fridkin, *Phys. Rev. Lett.* **2002**, *88*, 179701.
[9] A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin, A. Zlatkin, *Nature* **1998**, *391*, 874.
[10] N. Eidelman, C. G. Simon, *J. Res. Natl. Inst. Stand. Technol.* **2004**, *109*, 219.
[11] N. Tsutsumi, A. Ueyasu, W. Sakai, C. K. Chiang, *Thin Solid Films* **2005**, *483*, 340.
[12] K. J. Kim, S. L. Hsu, *Polymer* **1994**, *35*, 3612.
[13] H. S. Xu, *J. Appl. Polym. Sci.* **2001**, *80*, 2259.
[14] Q. M. Zhang, H. S. Xu, F. Fang, Z. Y. Cheng, F. Xia, H. You, *J. Appl. Phys.* **2001**, *89*, 2613.
[15] K. Tashiro, M. Kobayashi, *Spectrochim. Acta, Part A-Molecular and Bimolecular Spectroscopy* **1994**, *50*, 1573.
[16] K. Kimura, K. Kobayashi, H. Yamada, T. Horiuchi, K. Ishida, K. Matsushige, *Appl. Phys. Lett* **2003**, *82*, 4050.

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