A study of the optical and electronic properties of poly (vinylidene fluoride–trifluoroethylene) copolymer thin films

Y.X. Li a,b, L. Yan b, R.P. Shrestha b, D. Yang b, Z. Ounaies c, E.A. Irene b,*

a School of Physics and Microelectronics, Shandong University, Jinan, Shandong, 250100, China
b Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA
c Department of Aerospace Engineering, Texas A&M University, 3141 TAMU College Station, TX 77843-3141, USA

Received 12 December 2005; received in revised form 20 January 2006; accepted 20 January 2006

Abstract

Thin films of poly(vinylidene fluoride–trifluoroethylene) copolymer were prepared by spin casting from methylethylketone solutions onto SiO2, Si, and quartz slides substrates. The films were optically transparent in the 1.5–4.5eV (830–280nm) photon energy range and found to be uniform and smooth as determined using near ultraviolet–visible spectrum and atomic force microscopy, respectively. A Cauchy model was used to fit spectroscopic ellipsometry (SE) data to obtain the refractive index in 1.5–4.5eV (830–280nm) that was found to decrease for thinner films. SE performed at several sensitive angles of incidence has revealed slight optical anisotropy for films thicker than 120nm. Annealing in vacuum densified the films as evidenced by an increase in the refractive index and a decrease in the film thickness. Capacitance versus voltage measurements revealed a static dielectric constant of about 7.5.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Poly(vinylidene fluoride–trifluoroethylene); Ellipsometry; Optical properties; Static dielectric constant

1. Introduction

The copolymer of vinylidene fluoride with trifluoroethylene [P(VDF–TrFE)] has been widely studied for over 35 years since the discovery that this material exhibited piezoelectricity [1] and pyroelectricity [2] in P(VDF, and ferroelectricity in P(VDF–TrFE) [3]. These properties led to a broad range of applications [4–7] for this material in electromechanical and microelectromechanical systems, such as ultrasound and audio frequency transducers, sensors, actuators, etc. As a ferroelectric material P(VDF–TrFE) copolymer can be electrically switched between its two stable polarization states, and therefore can be used in high-density nonvolatile random-access memories [8,9]. For nonvolatile memory with a nondestructive readout capability and a smaller cell size, a memory structure based on metal-ferroelectric-semiconductor field-effect transistor has shown promise. Accurate optical properties and film thickness of the P(VDF–TrFE) copolymer as ferroelectric thin films are crucial for the fabrication and understanding the organic electronic and optical devices and these properties are therefore the focus of this study.

The optical properties of P(VDF–TrFE) copolymer films have been studied both experimentally [10–12] and theoretically [13,14]. Typically the published studies used thick films (>1μm), and measured film thicknesses using step height methods that are inaccurate for thin organic films. Optical properties have also been determined for thin films of P(VDF–TrFE) copolymer that have been prepared by the Langmuir–Blodgett (LB) method, that yielded highly oriented polycrystalline films with polymer chains parallel to the film and thus with uniaxial anisotropy [10]. At this time no studies have been reported to determine the optical properties of thin P(VDF–TrFE) copolymer films made by the spin casting method that will likely produce films that are less dense and anisotropic.

The present study focuses on the optical properties of P(VDF–TrFE) copolymer that is 50mol% PVDF and 50mol% TrFE and that is spin-cast film up to 250nm film thickness and studied using variable angle spectroscopic ellipsometry (SE) over the photon energy range 1.5–4.5eV (830–280nm). The complex dielectric function (N(λ)=n(λ)+ik(λ) where n(λ) is the refractive index and k(λ) the absorption index) and the film thickness were extracted
by fitting the experimental data to a parametric model of the sample, and vacuum annealing and optical anisotropy results are also reported. Capacitance versus voltage (C–V) measurements was performed on capacitor structures in order to determine the static dielectric constant $K$.

2. Experimental procedures

P(VDF–TrFE) copolymer in molar ratio of 50/50 was obtained from Atochem Inc. Solutions of 0.3–4.0 wt.% of the copolymer dissolved in methylethylketone (MEK) were used for spin coating films on quartz slides (Chemglass), single crystal Si and SiO$_2$ (from oxidized Si at 1000°C in pure O$_2$) substrates using spin speeds from 2000 to 8000 rpm and yielding film thicknesses from about 8.6 to 249.8 nm. The substrates were cleaned using standard RCA procedure [15] prior to deposition and the Si substrate also received an HF dip. Film annealing was done at 120°C in a vacuum of $\sim 7 \times 10^{-4}$ Pa, in order to investigate the effect of temperature on the optical properties and thickness. Films deposited on quartz slides were used to obtain absorbance near ultraviolet–visible (UV–Vis) spectra using a LAMBDA 950 Spectrophotometer. The film morphology and surface roughness were determined using a Multimode IIIa Atomic Force Microscopy (AFM) and reported in an area of $2 \times 2 \mu$m$^2$.

The dispersion of the refractive index $n(\lambda)$ and absorption index $k(\lambda)$ and the thickness of copolymer films were obtained by fitting the measured ellipsometric parameters $\Psi(\lambda, \phi)$ and $\Delta(\lambda, \phi)$ to an optical model using J.A. Woollam Inc. analysis software (WVASE32) [16], where $\Psi(\lambda, \phi)$ is the amplitude change between the p-(parallel to the plane of incidence) and s-(perpendicular to the plane of incidence) components of the polarized light that occurs during reflection, and $\Delta(\lambda, \phi)$ is difference in the phase. These measurables were collected in the spectral range 1.5–4.5 eV (830–280 nm) using a custom built variable angle rotating analyzer spectroscopic ellipsometer and a J.A. Woollam Co. model M88 spectroscopic ellipsometer. $\Psi(\lambda, \phi)$ and $\Delta(\lambda, \phi)$ are related to the complex reflection coefficient $\rho(\lambda, \phi)$ and to the ratio of Fresnel coefficients $R_p(\lambda, \phi)$ and $R_s(\lambda, \phi)$ by the formula $\rho(\lambda, \phi) = R_p(\lambda, \phi)/R_s(\lambda, \phi) = \tan(\Psi(\lambda, \phi)) e^{i\Delta(\lambda, \phi)}$ [17].

The Cauchy model was chosen to represent the optical properties of the P(VDF–TrFE) films which are shown below to be optically transparent in the UV–Vis range. The Cauchy formula [17] used is as follows:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

(1)

Where $\lambda$ is the wavelength and $A$, $B$, and $C$ are parameters that are fit in the analysis. A regression analysis was performed to fit the experimental data to the model. The differences between the model and the experimental data were expressed by the mean-squared error (MSE) which is defined as follows [16]:

$$\text{MSE} = \frac{1}{2N-M} \sum_{i=1}^{N} \left( \frac{\Psi_{i}^{\text{mod}} - \Psi_{i}^{\text{exp}}}{\sigma_{\Psi_{i}}^{\text{exp}}} \right)^2 + \left( \frac{\Delta_{i}^{\text{mod}} - \Delta_{i}^{\text{exp}}}{\sigma_{\Delta_{i}}^{\text{exp}}} \right)^2$$

(2)

Where $N$ is the number of $\Psi(\lambda, \phi)$ and $\Delta(\lambda, \phi)$ pairs used, and $M$ is the number of parameters varied in the regression analysis, while $\sigma$ is the standard deviation of the experimental data points. The smaller the MSE, the better the agreement of

![Fig. 1. UV–Vis absorption spectrum of ~20nm spin cast P(VDF–TrFE) film on a quartz slide substrate.](image-url)
experimental and model generated results. In order to reduce the correlation among the fitted parameters and improve thickness precision, ellipsometric data were recorded at different angles of incidence ($\phi = 65^\circ, 70^\circ, 75^\circ$) in the investigated spectral range and multi sample data analysis was used. In addition, results from independent techniques such as UV–Vis spectroscopy and AFM images were used as input to the models. Optically anisotropy of P(VDF–TrFE) films was checked by rotating samples in the plane of the substrate to determine in plane anisotropy and at various incident angles to determine out of film plane anisotropy.

Capacitor structures were prepared by evaporating Al through a shadow mask onto P(VDF–TrFE) films that were deposited onto SiO$_2$ grown on Si substrates. Capacitance–voltage measurements were performed using a combination HP 4284A LCR meter with a Keithley 236 as the voltage source at high frequency (1 MHz, 20mV oscillator levels).

3. Results and discussion

3.1. Optical model

Representative UV–Vis spectroscopy results are shown in Fig. 1 for a P(VDF–TrFE) thin film deposited on a quartz slide substrate. It is seen that the P(VDF–TrFE) films display very low absorption in the SE range to be used and can be approximated as being optically transparent in the 1.5–4.5 eV (830–280 nm) range. A Cauchy dispersion formula given above was therefore chosen to represent the optical properties of our P(VDF–TrFE) films.

P(VDF–TrFE) films were deposited on bare silicon and on thin (native oxide $\leq$ 1 nm) and thick SiO$_2$ (about 60 nm). The SiO$_2$ thickness was first determined and then after deposition the P(VDF–TrFE) film thickness and refractive index were measured.
determined using a Cauchy model. Typical SE data from three P(VDF–TrFE) samples of about the same thickness (slightly greater than 70nm) and each on a different substrate are shown in Fig. 2 along with model generated data. The fit is seen to be good with low MSE values (given in the caption of Fig. 2). The refractive indices extracted from the above SE regression analysis are shown in Fig. 3. The observed variation of the index is likely due to the low optical contrast between P(VDF–TrFE) ($n$ about 1.4) and SiO$_2$ ($n$ about 1.5) films and that small errors in the SiO$_2$ thickness will yield larger variation in the extracted P(VDF–TrFE) index and thickness, and this effect is larger for thicker SiO$_2$ films as is seen in Fig. 3. This ellipsometry effect is due to the relative thicknesses of the films in the stack and not to any materials properties.

In order to determine the effects of film roughness on the extracted optical properties AFM was performed. Fig. 4a and b are typical AFM images of P(VDF–TrFE) films with thickness 8.6nm and 249.8nm respectively and the root mean squared (RMS) roughness of about 0.4nm for the 8.6nm film and 1.3nm for the 249.8nm or about 4% and 0.5% of the total thickness of the thin films, respectively. For films thinner than 20nm, the surface roughness will cause about 0.3nm decrease in thickness and 0.004 increase in refractive index when the roughness is approximated using a Bruggeman effective medium approximation (BEMA) layer (a mixed composition layer with 50% P(VDF–TrFE) and 50% voids and with a thickness of about 1.4 times the RMS roughness) on top of the P(VDF–TrFE) layer. But there will be only 0.0009 increase in refractive index and 0.96nm decrease in thickness by adding the BEMA roughness layer to the optical model for a 249.8nm thick P(VDF–TrFE) film. Fig. 5 shows the difference between the refractive indices obtained with and without the BEMA layer for a 8.6nm P(VDF–TrFE) film. It is concluded that the roughness layer does not need to be included in the optical properties determination except for films thinner than 20nm when the highest accuracy is desired.

3.2. Optical anisotropy

Ellipsometry has recently been used to investigate the optical anisotropy of thin polymer films [18–20]. Fig. 6 (from ref [18])
shows that polymer chains that lie in the plane of the film can lead to uniaxial anisotropy, and if the chains are also ordered in the plane of the film biaxial anisotropy results. Out-of-plane uniaxial anisotropy has been reported for LB P(VDF–TrFE) copolymer [10] and other polyfluorene films [21] indicating that the chains lie disordered in the plane of the film.

In-plane anisotropy of spin-cast P(VDF–TrFE) films was investigated using SE at different azimuth angles in-plane $-0^\circ$, $60^\circ$ and $150^\circ$ by rotating the sample in the plane of the film. SE data were obtained on the same spot of the film at incident angle $\phi=70^\circ$. The results shown in Fig. 7 indicate that the three sets of data are almost identical within the error limits indicating that there is no significant in-plane anisotropy in our spin-cast P(VDF–TrFE) films.

In order to determine out of plane anisotropy, SE was performed at multiple angles of incidence ($\phi$) from $65^\circ$ to $75^\circ$ in $5^\circ$ intervals. The choice of these angles was made according to the calculated $\Delta-\Psi$ trajectory which is used to evaluate the sensitivity of $\Psi$ and $\Delta$ to the incident angle. Fig. 8 showed the calculated $\Delta-\Psi$ trajectories at 1.96eV (632.8nm) photon energy with $\phi$ values from $60^\circ$ to $75^\circ$ and with P(VDF–TrFE) thicknesses from 1 to 320nm at 2nm intervals. The changes in $\Delta$ and $\Psi$ indicate that the most sensitive $\phi$ values were $65^\circ$–$75^\circ$ which were therefore selected for use in this study.

Fig. 11. Refractive indices ($n$) of 127.4nm P(VDF–TrFE) film as-deposited and annealed 3h at 120°C and 104nm P(VDF–TrFE) film annealed 72h up to 155°C in $\sim 7 \times 10^{-4}$ Pa vacuum system.

Fig. 13. The thickness dependence of the refractive indices ($n$) at 1.96eV (632.8nm) and 3.0eV (415nm).

Fig. 9 presents the experimental $\Psi$ and $\Delta$ values at the $\phi$ above with Cauchy isotropic fits for 140.7nm P(VDF–TrFE) film deposited on 53.1 nm SiO$_2$ on Si substrate. In this case, the MSE was 15.4. However, when a uniaxial anisotropic fit was used the MSE was lowered to 5.1. The refractive indices $n$ extracted from fitting SE data using isotropic model respectively recorded at incident angles $\phi$ from $65^\circ$ to $75^\circ$ are shown in Fig. 10. The difference of $n$ at 3.0eV (415nm) between $65^\circ$ and $75^\circ$ is 0.0033. We did not detect significant out-of-plane anisotropy for films less than 120nm.

3.3. Annealing studies

It was reported that thermal annealing under vacuum can remove the residual solvent and also improve the crystallinity of P(VDF–TrFE) [22]. Fig. 11 represents the change of refractive index $n$ for a 127nm P(VDF–TrFE) film deposited on 42nm SiO$_2$ on Si after annealing for 3h at 120°C and at $\sim 7 \times 10^{-4}$ Pa. An increase in $n$ of about 0.013 is measured at an incident photon energy of 3.0eV (415nm) and a decrease of 2.4nm (2%) in thickness. Another P(VDF–TrFE) film of similar thickness (104nm on 41nm SiO$_2$) annealed 72h in vacuum from room temperature to 155°C showed $n$ increasing 0.02 and thickness decreasing 3.4nm (3.3%) and is also displayed in Fig. 11. A comparison of the two samples indicates an initially relatively fast change with annealing but with a longer time to full...
densification. The small difference in slope between these two samples is due to the (P(VDF–TrFE) film thickness difference and will be discussed below.

3.4. Thickness dependence

SE was performed on (P(VDF–TrFE) films with different thicknesses. The extracted refractive indices n shown in Fig. 12 indicate that overall n increases with an increase in thickness. In addition, the change with thickness is greater in the thin film regime. This is more easily seen with Fig. 13 that shows the variation of n at 1.96eV (632.8nm) and 3.0eV (415nm) with thickness. This result may indicate a densification that results in improved crystallinity as was recently reported for thin polystyrene-derived films that showed that the degree of crystallinity depended strongly on the film thickness [23–25].

4. Dielectric constant measurement

The static dielectric constant was measured for Al/P(VDF–TrFE)/SiO2/Si samples of varying thicknesses. Fig. 14 shows a typical C–V curve for a 152nm P(VDF–TrFE) film on 53.9nm SiO2 on n-type Si. Based on this ellipsometric thickness, the dielectric constant of P(VDF–TrFE) was calculated to be 7.5 according to the formula 1/C_{tot} = 1/K_{ox} – ε0A/L_{ox} + 1/K_{p} – ε0A/L_{p}, where C_{tot} is total capacitance, K_{ox}, L_{ox} are the dielectric constant and thickness of SiO2, and K_{p}, L_{p} are dielectric constant and thickness of P(VDF–TrFE). Another piece of the same sample was annealed for 3h in vacuum at 120°C and a value of 7.4 was obtained indicating that annealing has no significant effect on static dielectric constant. The value of about 7.5 measured for spin cast P(VDF–TrFE) films is lower than the reported value of ~10 for thicker films (>20μm, referred to as bulk material) [26,27].

5. Conclusions

Optical properties of P(VDF–TrFE) films deposited on different substrates were determined using variable angle spectroscopy ellipsometry in 1.5–4.5eV (830–280nm) photon energy. A Cauchy model was used to yield a good regression analysis fit. Different substrates do not significantly affect the refractive index which does decrease with thinner films. Variable angles (in plane and out of plane spectroscopic ellipsometry) revealed no in-plane anisotropy, but slight out-of-plane anisotropy for films thicker than 120nm. An increase in refractive index and decrease in thickness were found by annealing films in vacuum. The static dielectric constant K of about 7.5 was measured from C–V measurements.

Acknowledgment

This work was supported in part by the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award No. NCC-1-02037.

References