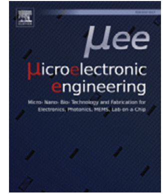
Microelectronic Engineering 171 (2017) 37–43

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee



Research paper

Spectroscopic ellipsometry study of spin coated P(VDF-TrFE-CTFE) thin films and P(VDF-TrFE-CTFE)/PMMA blends

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ARTICLE INFO

Article history:
Received 9 August 2016
Received in revised form 10 January 2017
Accepted 25 January 2017
Available online 27 January 2017

Keywords:
Polymer thin films
Polymer MEMS
Spectroscopic ellipsometry
Electroactive polymers
Optical characterization

ABSTRACT

The optical properties of spin coated P(VDF-TrFE-CTFE) electrostrictive polymer films and films of a novel blend of P(VDF-TrFE-CTFE) with Poly(methyl methacrylate) (PMMA) were studied by means of Variable Angle Spectroscopic Ellipsometry (VASE) in the wavelength range of 200-1000 nm and at 65°–75° incident angles using Cauchy and Sellmeier dispersion models. Such polymers are used as building blocks for polymer microelectromechanical systems (MEMS) and their integration with conventional processing requires an accurate and reproducible monitoring of their thickness and optical properties. The films were also characterized electrically and their breakdown fields were 1.20 MV/cm for the P(VDF-TrFE-CTFE) films and 1.76 MV/cm, for the P(VDF-TrFE-CTFE)/PMMA blend films. We report on significant changes in film texture between the two types of films. Our main finding is that optical anisotropy appears in both films and we have characterized this anisotropy for both electroactive polymers. The blend films display a higher refractive index in the plane of the film while the homogenous P(VDF-TrFE-CTFE) display a higher refractive index in the direction perpendicular to the plane. Depolarization and scattering were analyzed with the Mueller-Stokes formalism and a depolarization correction method was implemented decoupling thickness related non-uniformity from scattering effects. It is concluded that in-line, non-destructive characterization tools presented here are useful for both the industrialization of P(VDF-TrFE-CTFE) based micro-electro-mechanical systems and for probing the correlation between surface morphology and optical properties using VASE.

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1. Introduction

The terpolymers of polyvinylidene fluoride (PVDF), P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE), have been extensively studied and developed over the past decade as an electrically activated polymeric actuator material due to their relaxor ferroelectric behavior which features large electrostrictive strains and a high energy density [1–3]. Longitudinal and transverse strains larger than 7% and 4.5% respectively, along with a relatively high Young's modulus > 0.3 GPa [1], have been obtained for these semi-crystalline terpolymers, making them attractive for the production of MEMS sensors and actuators [2,3]. In addition, optical transparency and a large electro optical effect make these polymers good candidates for various optical applications such as micro-opto-electro-mechanical systems (MOEMS) [4].

Micron scale layers of P(VDF-TrFE-CTFE) are typically formed by spin-coating, while patterning can be performed using nano-imprint lithography (NIL) [5–7] or reactive ion etch (RIE) [8,9]. The electroactive polymer (EAP) is typically layered between two thin film conductors, allowing for the application of an electric field across the film, which results in a contraction of the film. The conductors are typically metals that can be deposited on either side of the polymer films, forming electrodes for functional, electrically activated devices [6,8]. Custom processing methods towards integrating those polymers with conventional fabrication technologies have been presented recently together with the characterization of the electrical and mechanical properties of structures made of those materials [5–7]. One problem facing single layer devices is the relatively high operation voltages, which are on the order of 150 V per micron of thickness. One way to tackle this problem in the case of field-activated EAPs, is to fabricate multilayer devices comprised of thin polymer films layered between electrodes to allow for lower voltage operation. Multilayer polymeric devices can be especially useful when combined with conjugate polymers or other softer electrode materials for fully flexible MEMS. These new methodologies towards "all polymer" structures for polymer MEMS will, however, increase device complexity. Multilayered structure fabrication requires in-line nondestructive thickness monitoring. This can be performed by either interferometry or ellipsometry using conventional tools. One key issue, as will be shown later, is that the terpolymer has anisotropic optical parameters which require better models and careful analysis for process control. In this paper we focus on ellipsometry of the

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http://dx.doi.org/10.1016/j.mee.2017.01.030
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terpolymer thin films, especially in defining the challenges and providing models for the polymer itself as well as for its polymer blend with PMMA.

Ellipsometry is a useful, non-destructive tool for characterizing the optical properties of thin films and both for in-line and off-line thickness monitoring and control. Due to its flexibility and precision, ellipsometry has been used as a characterization tool for a number of applications. Beyond thickness and refractive index, ellipsometry has been applied to the study of composition, crystallinity, roughness, doping concentration, and other material properties [10,11].

Optical properties are expressed by the complex dielectric function

$$n^*(\lambda) = n(\lambda) + ik(\lambda) \tag{1}$$

where $n(\lambda)$ and $k(\lambda)$ are the refractive index and attenuation constant tensors, respectively, and λ is the wavelength of the incident beam. For ultimately flat, uniform films on a substrate with known refractive index, this value of n^* is enough. However, in reality EAP thin films present numerous challenges to ellipsometry due to morphological effects, surface roughness and anisotropy. Therefore, thin film EAPs often require more detailed analysis and complex modeling techniques [10, 11], which take into consideration other effects such as scattering and anisotropic optical properties.

Previous works have demonstrated the use of Variable Angle Spectroscopic Ellipsometry (VASE) for measuring the thickness and dispersion of Langmuir-Blodgett co-polymer and terpolymer films of PVDF, which are highly oriented and polycrystalline [14,15]. Other works have determined the optical properties of spin-coated P(VDF-TrFE) films [16] which are less ordered and show some optical anisotropy. Ellipsometry investigations performed on rough and scattering surfaces of ZnO present advanced methods that can be implemented to polymer films [17]. Development and industrialization of polymeric MEMS or MOEMS devices using P(VDF-TrFE-CTFE) and promising new polymer blends, requires their comprehensive characterization.

In this work, we present a methodical VASE investigation of spin coated P(VDF-TrFE-CTFE) films with thicknesses in the range of few microns which is characteristic to MEMS or MOEMS devices (200 nm–2 μm). The films are both anisotropic and possess depolarizing properties; thus, they require the use of advanced generalized ellipsometry methods and the Mueller-Stokes formalism in order to find the best-fit model. In this paper, we present the use of these techniques to investigate the optical properties of both P(VDF-TrFE-CTFE) and for the (VDF-TrFE-CTFE)/PMMA blend films.

2. Experimental

The films were spin coated using the following protocols. First, terpolymer pellets (Piezotech VF2:61.3/VF3:29.7/CTFE:9%) were mixed with methyl ethyl ketone (MEK) to create 3% and 8% solutions by weight [5,6,7]. Next, to prepare P(VDF-TrFE-CTFE)/PMMA blends, 0.8 g PMMA (Sigma Aldrich, Israel) and 8 g P(VDF-TrFE-CTFE) were added to 100 g MEK [12].

The terpolymer solutions were spin-coated onto 4″ polished silicon (100) wafers and on 2″ × 2″ quartz slides (for transmittance measurements) at a rotation speed of 3000 rpm under ambient conditions. Next, the samples were placed in an atmospheric oven for a reflow process at 180 °C for 10 min to improve film quality and reduce porosity. Following this, the samples were cooled to room temperature and then annealed for an additional 4 h at 105 °C to increase crystallinity in the polymer [7].

A thin Cr layer (15 nm) was deposited on one P(VDF-TrFE-CTFE) and one P(VDF-TrFE-CTFE)/PMMA sample by RF sputtering with Argon (K575X, Quarum Technologies) in order to prevent the surface from charging while examining the surface morphology of the dielectric films with Scanning Electron Microscopy (SEM) (Quanta 200 FEG, FEI).

Ellipsometry measurements were performed using an M-2000 DUV spectroscopic ellipsometer (J.A Woollam) in the range of 200–1000 nm, resolution of 1.5 nm and at incident angels of 65, 70 and 75°. Transmittance measurements were performed using the same instrument with normal incidence, with the polymer thin film deposited on a quartz substrate (EMS, cat. # 72250-03).

The dispersion of the refractive index, n, and extinction coefficient, k, and the thickness of the films were obtained by fitting measured ellipsometric angles, ψ and Δ, to optical models using the WVASE32® analysis software by J.A Woollam. Where $tan\psi(\lambda,\varnothing)$ is the amplitude ratio between the parallel and the perpendicular components of the polarized light and $\Delta(\lambda,\varnothing)$ is the phase difference. ψ and Δ are extracted from the complex refraction coefficient and Fresnel coefficient by the formula [10,11]:

$$\rho(\lambda,\varnothing) = \frac{R_p(\lambda,\varnothing)}{R_s(\lambda,\varnothing)} = tan\psi(\lambda,\varnothing)e^{i\Delta(\lambda,\varnothing)} \tag{2}$$

The mean squared error (MSE) is used to assess the differences between the experimental data and the model. A lower MSE indicates better agreement with the results [10,11].

$$MSE = \frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\psi_i^{model}-\psi_i^{exp}}{\sigma_{\psi_i}^{exp}}\right)^2 + \left(\frac{\Delta_i^{model}-\Delta_i^{exp}}{\sigma_{\psi\Delta_i}^{exp}}\right)^2\right] \tag{3}$$

where N is the number of data pairs used, M is the number of parameters varied in the regression analysis and σ is the standard deviation of the data points.

The Cauchy and Sellmeier dispersion models were used to fit the refractive index while the extinction coefficient represented by the Urbach formula in both cases [18] (Table 1).

The effective optical constants of mixtures of two or more materials, ε, are calculated by Effective Medium Approximation (EMA) models. The Bruggeman EMA (BEMA) requires the numerical solution of Eq. (5) [10,11]:

$$\sum_i f_i \cdot \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} = 0 \tag{4}$$

where f_i and ε_i are the fraction volume and dielectric constant of material i respectively. The BEMA model was used for charactering P(VDF-TrFE-CTFE)/PMMA blends.

Anisotropy is common in spin coated polymer films due to the long range ordered chains that lie disordered in the plane of the film [16]. Anisotropy was investigated with advanced measurement options available with WVASE32. Uniaxial anisotropy models were used to obtain the directional refractive indexes $n_x = n_y \neq n_z$ for both the blend and the homogenous films.

Spin coated polymer films often exhibit rough surfaces composed of disordered chains and thickness non-uniformity. These issues pose a challenge to conventional ellipsometry measurement by creating

Table 1
Cauchy and Sellmeier models parameters [18].

Cauchy model	Sellmeier model
$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$	$n(\lambda) = \sqrt{A + \frac{B\lambda^2}{\lambda^2 - C^2} + \frac{D\lambda^2}{\lambda^2 - E^2}}$
$k(\lambda) = \alpha e^{\beta[\frac{hc}{q}\cdot(\frac{1}{\lambda}-\frac{1}{\gamma})]}$	$k(\lambda) = \alpha e^{\beta[\frac{hc}{q}\cdot(\frac{1}{\lambda}-\frac{1}{\gamma})]}$

Where, λ [μm] is the wavelength α [dimensionless] is the extinction coefficient amplitude, β [ev^{-1}], is the exponent factor γ [ev] is the band edge h is Plank's constant, c is the speed of light and q is the electron charge. For the Cauchy model, A [dimensionless], B [μm^2] and C [μm^4] are fitting parameters. For the Sellmeier model, A [dimensionless], B [dimensionless], C [nm], D [dimensionless] and E [nm] are the fitting parameters. Note that C and E are resonance wavelengths for which n diverges, thus the fit is valid for only inside the wavelength range between C and E but not at the boundaries (C & E).

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