Thin Solid Films 565 (2014) 72–78

Contents lists available at ScienceDirect

Thin Solid Films

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

Determination of thicknesses and refractive indices of polymer thin films by multiple incident media ellipsometry

Ufuk Karabiyik [a,*], Min Mao [a], Sushil K. Satija [b], Alan R. Esker [a]

[a] Department of Chemistry (0212), Virginia Tech, Blacksburg, VA 24061, USA
[b] Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

ARTICLE INFO

Article history:
Received 16 January 2014
Received in revised form 11 June 2014
Accepted 26 June 2014
Available online 4 July 2014

Keywords:
Refractive indices
Film thickness
Optical properties
Ellipsometry
Polymer
Thin films

ABSTRACT

Single wavelength ellipsometry measurements at Brewster's angle and in multiple incident media provide a powerful technique for characterizing ultrathin (<20–30 nm) polymer films. Only one ellipsometric parameter (i.e. amplitude ratio) is obtained at Brewster's angle since phase shift is 90°. By conducting the experiments in different ambient media, simultaneous determinations of a film's thickness and refractive index for ultrathin polymer films are possible at Brewster's angle. Poly(tert-butyl acrylate) (PtBA) Langmuir–Blodgett films serve as a model system for the simultaneous determination of thickness and refractive index (1.45 ± 0.01 at 632 nm). Thickness measurements on films of variable thickness agree with X-ray reflectivity results ±0.8 nm. The method is also applicable to spincoated films where refractive indices of PtBA, polystyrene and poly(methyl methacrylate) are found to agree with literature values within experimental error.

Published by Elsevier B.V.

1. Introduction

Precise control of film thickness is often a critical parameter in ultrathin polymer coatings. Several microscopy [1,2] and reflectivity [3,4] methods such as profilometry, atomic force microscopy (AFM), and X-ray reflectivity (XR) have been developed for measuring the thicknesses of polymer thin films in the nanometer regime. However, measurements should be rapid and non-destructive for researchers who require routine determinations of film thickness prior to further surface characterization. Ellipsometry is a rapid, non-contact, and non-destructive method for probing thickness and refractive index in nanoscale polymer coatings through changes in polarization upon the reflection of light from a surface [5]. The technique is applicable for both ex-situ measurements in air and in-situ experiments in liquid media. Like other reflectivity techniques, thickness determinations via ellipsometry are complicated by the need to know the film's optical properties. At Brewster's angle for very thin films (<20–30 nm) where the thickness is much smaller than a single wavelength of a laser light source (632.8 nm) the ellipticity equations are simplified and only one of the ellipticity parameters is known. Therefore, under these conditions it is not possible to uniquely obtain both thickness and refractive index through a single measurement at a constant wavelength for ultrathin films [6]. Spectroscopic ellipsometers overcome this problem by making measurements at multiple wavelengths under the assumption that the refractive index of the film can be optically modeled as a function of wavelength over the studied range. Making this assumption often requires some prior knowledge of the refractive index and absorbance properties of the film. This problem is further complicated by the fact that the bulk refractive indices may not be applicable for ultrathin interfaces with thickness <5 nm [7]. One way to circumvent this problem for single wavelength instruments is the use of multiple incident media (MIM). This technique has previously been applied to silicon surfaces with an oxide layer [8], self-assembled monolayers on silicon substrates [9–11], and water adsorbed on chromium slides [12].

The MIM technique requires two ambient media whose refractive indices should be significantly different from each other. The task of choosing the ambient media is complicated by the fact that the medium should be chemically and physically (non-swelling) inert. In addition, a liquid cell that is compatible with the variable angle setup must be constructed. The most common cell design described in the literature is trapezoidal in shape to ensure that the incident and reflected light enter and leave the cell at normal incidence, thereby avoiding changes in the polarization state. Other cell designs having hollow prism shapes have also been reported [12]. In this paper, a quartz cylinder sample cell (described in the Experimental section, Fig. 1) [11] has been used with a phase modulated ellipsometer to conduct the MIM measurements on polymer films. The advantage of the cylindrical cell design is that it

---

* Corresponding author. Tel.: +1 540 449 2564; fax: +1 717 217 8223.
E-mail addresses: ukarabiyik@arglobal.com (U. Karabiyik), mmao@vt.edu (M. Mao), sushil.satija@nist.gov (S.K. Satija), aesker@vt.edu (A.R. Esker).

http://dx.doi.org/10.1016/j.tsf.2014.06.050
0040-6090/Published by Elsevier B.V.

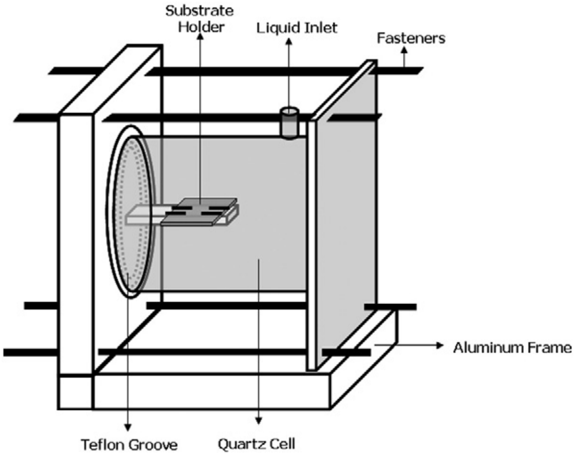

Fig. 1. Schematic representation of the multiple incident media (MIM) ellipsometry sample cell.

does not require a fixed incident angle, whereby Brewster's angle can be scanned easily provided that the cylindrical cell is properly centered with respect to the axis of rotation of the arms.

Like ellipsometry, X-ray reflectivity (XR) and neutron reflectivity (NR) can reliably measure a polymer film's thickness with Angstrom level resolution. For single component homogenous films with small surface roughnesses, the Kiessig fringe patterns unambiguously yield a film's thickness [13–15]. Comparative XR and spectroscopic ellipsometry studies can be found in the literature [16–18]. As shown in this study, the MIM method enables one to simultaneously determine the refractive index and thickness of a thin film. In this respect, MIM ellipsometry is comparable to the use of multiple ambient media and polarized neutrons to try to solve the phase problem in neutron reflectivity [19–24]. The advantage of the MIM ellipsometry technique over XR and NR is the fact that it can be done much more quickly (<5 min).

In this study the Langmuir–Blodgett (LB) technique [25] is used to transfer poly(tert-butyl acrylate) (PtBA) films onto solid substrates from a water subphase. PtBA LB-films are ideal for testing the MIM technique on polymer thin films because quantitative LB-transfer [26] by Y-type deposition yields films whose thicknesses linearly correlate with the number of deposited layers and films that do not swell in water [27]. Results obtained via MIM ellipsometry are then compared to XR results to validate the method. Finally, the technique is applied to spincoated systems of PtBA, polystyrene (PS), and poly(methyl methacrylate) (PMMA) to demonstrate general applicability.

2. Experimental section

2.1. Materials

The following compounds were used without further purification: PtBA (number average molar mass, $M_n = 23$ kg·mol^{-1}; polydispersity index, $M_w/M_n = 1.08$) and PS ($M_n = 604$, 76, and 23 kg·mol^{-1}; $M_w/M_n = 1.05$, 1.04, and 1.05, respectively) were obtained from Polymer Source, Inc. and PMMA ($M_n = 107$ kg·mol^{-1}, $M_w/M_n = 1.1$) was obtained from Polymer Laboratories, Ltd. [28]. Chloroform (HPLC grade, EMD Chemicals) was used to prepare ~0.5 mg·g^{-1} PtBA solutions for LB-deposition. Spincoated films were prepared from polymer solutions of different weight percent concentrations (wt.%) in toluene (HPLC grade, EMD Chemicals). The water used in all steps of the experiments was ultrapure water (18.2 MΩ, Millipore, MilliQ Gradient A-10, <10 ppb organic impurities). In addition, ethylene glycol (EG), triethylene glycol (TEG), (reagent plus, >99%, Sigma-Aldrich), and glycerol (ultrapure, HPLC Grade, Alfa-Aesar) were used as different ambient media. All other reagents, H_2O_2 (30% by volume), H_2SO_4 (conc.), and NH_4OH (28% by volume) were purchased from EM Science, VWR International, and Fisher Scientific, respectively. Silicon wafers (100) were purchased from Waferworld, Inc.

2.2. Film preparation

Silicon wafers were used for both LB and spincoated films. Substrates for spincoating were cut into roughly 15 × 15 mm^2 pieces. LB-films were prepared on 40 × 40 mm^2 substrates. Following the XR experiments, LB-films were cut into 15 × 15 mm^2 pieces for ellipsometry. All substrates were cleaned in a 5:1:1 (by vol.) mixture of H_2O:H_2O_2:NH_4OH for 1 h. After the substrates were rinsed with Millipore water and blown dry with nitrogen, the substrates were placed in a 7:3 (by vol.) mixture of H_2SO_4:H_2O_2 for 3 h. The substrates were then rinsed with copious amounts of water, dried with nitrogen, and were dipped into buffered HF solutions (J. T. Baker) for 5 min followed by a short dip into a buffered NH_4F (J. T. Baker) solution to obtain hydrophobic silicon substrates. PtBA LB-films were prepared on a standard LB-trough (KSV 2000, KSV Instruments, Inc.) resting on a floating table inside a Plexiglas box. The temperature of the subphase (Millipore water) was maintained at 22.5 °C by a water circulation bath. Surface pressure, Π, was monitored via the Wilhelmy platetechnique. The trough was filled with Millipore water and the PtBA spreading solution was spread to $\Pi = 8$–12 mN·m^{-1}; i.e. below the transfer pressure to avoid multilayer formation. The transfer $\Pi = 18.5$ mN·m^{-1} was approached with a compression rate of 10 mm·min^{-1} and the maximum forward and reverse barrier speeds were 10 mm·min^{-1}. The dipping rate of the substrate for both up and downstrokes was set to 10 mm·min^{-1}. Transfer proceeded by Y-type deposition to prepare multilayer films of PtBA. All spincoated films were prepared from polymer solutions in toluene and were spun onto hydrophobic silicon wafers at 2000 rpm for 60 s.

2.3. Ellipsometry

Ellipsometry measurements were carried out with a phase modulated ellipsometer (Beaglehole Instruments, Wellington, New Zealand) at a wavelength of 632.8 nm (HeNe laser) at Brewster's angle. The sample cell is depicted in Fig. 1. Measurements in air were performed at several different positions in order to confirm the uniformity and the quality of the films through the quartz cell. Measurements with water as the ambient medium were performed in the same quartz cell. The design of the quartz cell allows us to fill the sample cell with liquid after completing the air measurements without removing the substrate, thereby allowing measurements on the same position of the wafer. One concern with a cylindrical quartz cell is anisotropy of its refractive index. For our cell, we find that we obtain similar film thicknesses and refractive indices for thick films measured in air by spectroscopic ellipsometry (SE) and multiple angle of incidence (MAOI) ellipsometry measurements. Moreover we find excellent agreement between ellipsometry and X-ray reflectivity measurements [26,27].

The fundamental equation for the reflection coefficient in ellipsometry is [29,10]:

$$\mathrm{r} = \frac{\mathrm{r_p}}{\mathrm{r_s}} = \mathrm{Re(r)} + \mathrm{iIm(r)} = \tan\Psi \exp(\mathrm{i}\Delta) \qquad (1)$$

where r_p and r_s are the reflection coefficients for p and s polarized light, respectively, and Ψ and Δ are the ellipsometric parameters. At Brewster's angle, $\mathrm{Re(r)} = 0$, which is equivalent to $\Delta = 90°$. Under these conditions, Eq. (1) simplifies to [30]:

$$\rho = \mathrm{r} = \frac{\mathrm{r_p}}{\mathrm{r_s}} = \mathrm{iIm(r)} = \tan\Psi \qquad (2)$$