Morphology and Spectroscopic Ellipsometry of PMMA Thin Films

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Abstract

The morphology and optical properties of PMMA thin films deposited on silicon substrates were investigated. The spin coated films were characterized by atomic force microscopy and spectroscopic ellipsometry. Regardless that, the samples were deposited at different coating speeds, the surface structures of all PMMA thin films were consistent, and found to be relatively smooth, with a mean grain size in the range of 13-25 nm. The refractive index as well as the extinction coefficient of the films was determined using spectroscopic ellipsometry data over the wavelength range 380-750 nm. For this purpose, we used the Cauchy dispersion relation in order to represent PMMA layers, and then models were built by adding a roughness layer, which simply corrects any possible deviation from planarity. Besides, the thicknesses of all four films were calculated simultaneously based on multiple sample analysis method. By using this method, optical properties were coupled in such way that, the optical constants for all samples were assumed to be identical.

Keywords: optical properties, PMMA thin films, surface morphology, spectroscopic ellipsometry, multiple sample analysis

1. Introduction

Polymethylmethacrylate (PMMA) is considered as a member of a huge family of methacrylate esters. Its physical properties make it a promising candidate for many applications. In addition, it is a light weighted material when compared to glass as their density is much less than that of glass (1.17–1.20 g/cm^3) (Acrylic Plastic Sheet 2002). Besides, its impact strength is higher than both glass and polystyrene. However, PMMA's impact strength is significantly lower than polycarbonate and some engineered polymers. Furthermore, PMMA transmits up to 92% of visible light with reflection about 4% (3 mm thickness) from each of its surfaces. This high transmittance and low reflections is directly correlated to PMMA refractive index (1.4905 at 589.3 nm). Moreover, like ordinary window glass, PMMA filters ultraviolet (UV) light at wavelengths below 300 nm (Acrylic Plastic Sheet 2002).These marvelous and unusual properties of PMMA make them as a good synthetic material for many applications such as optical communications, polymer optical fibers, optical waveguides, optical connectors, optical storage systems (Atef, Swoboda, & Zimmermann, 2010a,b; Guo et al., 2003) and optical switches with low driving power (Cao et al., 2012). Furthermore, PMMA thin films play a crucial role in technological applications including coatings, adhesives, lithography to organic light emitting diodes as well as various organic material based devices, such as sensors. Therefore, studying the optical properties of such material through methodological characterization merits further investigations.

One of the optical methods used to achieve this goal is spectroscopic ellipsometry (SE). In SE method, whereas, all films optical constants are calculated based on two measured quantities Psi (Ψ) and Delta (Δ). While Ψ is the ratio of the field amplitudes intensity of the two wave components, Δ is the phase difference between the p and s -waves induced by reflection from the thin film sample. Both Ψ and Δ are given by the equations below (Azzam & Bashara, 1987):

$$\tan \Psi = \left| r_p \right| / \left| r_s \right| \tag{1}$$

$$r_p / r_s = \exp(i\Delta).\tan \Psi \tag{2}$$

Where, r_p and r_s are the complex Fresnel reflection coefficients for p and s polarizations, respectively. Whereas, Ψ and Δ allow to determine both the film thickness and the spectral dependencies of optical constants. In order to convert Ψ and Δ values to well-known parameters such as; refractive index, extinction coefficient, and film thickness, a fitting procedure is used to calculate these parameters. However, to generate Ψ and Δ parameters few steps must be done. First of all, a model is built by assuming the film structure with some optical properties. Then, the model is modified by a fitting algorithm in order to minimize the difference between the generated and measured data. . This difference is evaluated using mean square error (MSE) given by equation 3 (Tompkins, 2006):

$$MSE = \left[\frac{1}{2N - P} \sum_{i=1}^{N} \left(\left(\frac{\Psi_i^m - \Psi_i^g}{\sigma_i^{\Psi}} \right)^2 + \left(\frac{\Delta_i^m - \Delta_i^g}{\sigma_i^{\Delta}} \right)^2 \right) \right]^{1/2} \qquad (3)$$

Both Ψ_i and Δ_i represent the measured Ψ and Δ angles at the ith wavelength and δ is the standard deviation. While upper indices m and g denote the measured and generated data, respectively, N and P represent the number of measured values and fitted parameters, respectively. Hence, SE utilizes a model based method for determining thin film thickness, surface roughness, refractive index as well as extinction coefficient. However, finding a film dielectric function along with the film thickness is not an easy task. Therefore, multiple sample analysis (MSA) was used as a solution to overcome such difficulty. The main idea behind this method is that the optical properties of unknown layer are identical in many samples regardless their thickness. Therefore, the ability of getting the dielectric function is related with defining more samples with the same optical constants coupled across all samples.

Farrendahi and Arwin (1998) have employed multiple sample analysis approach to find dielectric functions, film thicknesses and films surface roughness of Ta_2O_5, ScN, and CeO_2. Besides, Heinemeyer et al. (2008) utilized MSA to focus on uniaxial anisotropy of organic thin films, while other research groups have reported optical constants for silicon and thermally grown silicon oxide over the energy range of 0.75-6.5 eV (Herzinger et al., 1998), band gaps for W oxides and Ni oxides (Valyukh et al., 2009) and optical properties evaluation for the fluorocarbon films plasma deposited on silicon substrates (Easwarakhanthan et al., 2007). In this study, we aim to study the morphology of different PMMA thin films with different thicknesses deposited by spin coating on silicon substrates. We will employ SE and MSA approach to find the optical constants and thicknesses for these films.

2. Experimental

An amount of 0.1 g poly (methyl methacrylate) (PMMA) purchased from Fluka-Aldrich, with linear formula $[- CH_2C(CH_3) (CO_2CH_3) -]_n$ was dissolved in 20 mL of high purity chlorobenzene. The solution was then filtered using 0.5 μm filters to remove any non-dissolved impurities and dust before use. Before film deposition the silicon substrates (100) were carefully cleaned using acetone, isopropyl alcohol solution, and distilled water, sequentially. After cleaning the samples, the pre-cleaned substrates were dried with argon. All films were prepared by spin coating, whereas, a spin coating method will produce a centripetal force, which leads to spread the material on the substrate surface and as a result a thin film will form. The final film properties (thickness, roughness, uniformity, etc.) depend on the material type and other parameters such as rotating speed, concentration, viscosity, drying rate and surface tension. In order to identify films physical properties, we have prepared PMMA thin films in 4 different spin coating speeds (600, 800, 1000, and 1200 rpm) while other parameters were kept fixed. Then, the prepared films were directly transferred into an oven to dry them up at 100°C for 1h. A Nanoscope IIIA atomic force microscope (AFM), operating in the tapping mode was used in air at room temperature to visualize the films surface morphology, with the aid of a scanner that equipped with a Si cantilever with maximum scan range of 5μm ×5μm. Furthermore, the Gwyddion software package was used to analyze the AFM images. On the other hand, spectroscopic ellipsometry (SE) was performed using variable angle spectroscopic ellipsometer (VASE) in order to acquire the ellipsometric parameters Ψ and Δ in air at room temperature over the wavelength range 380-750 nm in steps of 2.5 nm at incidence angles 65°. And finally, the spectroscopic ellipsometry data were fitted using software WVASE32® implemented in the ellipsometer.

3. Results and discussions

AFM images were acquired for the four PMMA thin films in order to obtain important information on morphology, and accordingly to evaluate the height distributions and the thin films roughness. Figure 1 shows AFM images for PMMA spin coated films at four different coating speeds. The features of the collected peaks with different heights, groves, and relatively small irregularities is a clear indication that the grains is randomly oriented (refer to Figure 1), with no clear changes between all films. The quantitative analysis of these images imply that the root mean

square (RMS) roughness for the first sample film (600 rpm) PMMA thin film is 0.863 nm, 0.761 nm for the second film (800rpm), 0.701 nm for the third film (1000 rpm), and 0.635 nm for the forth film (1200 rpm). However, the grains distributions in all films were almost the same with average grain size of 13-25 nm. This could be correlated to the films surface structures similarities, whereas, our results here are consistent with other previous investigations (Nyl et al., 2012; Ismail et al., 201).
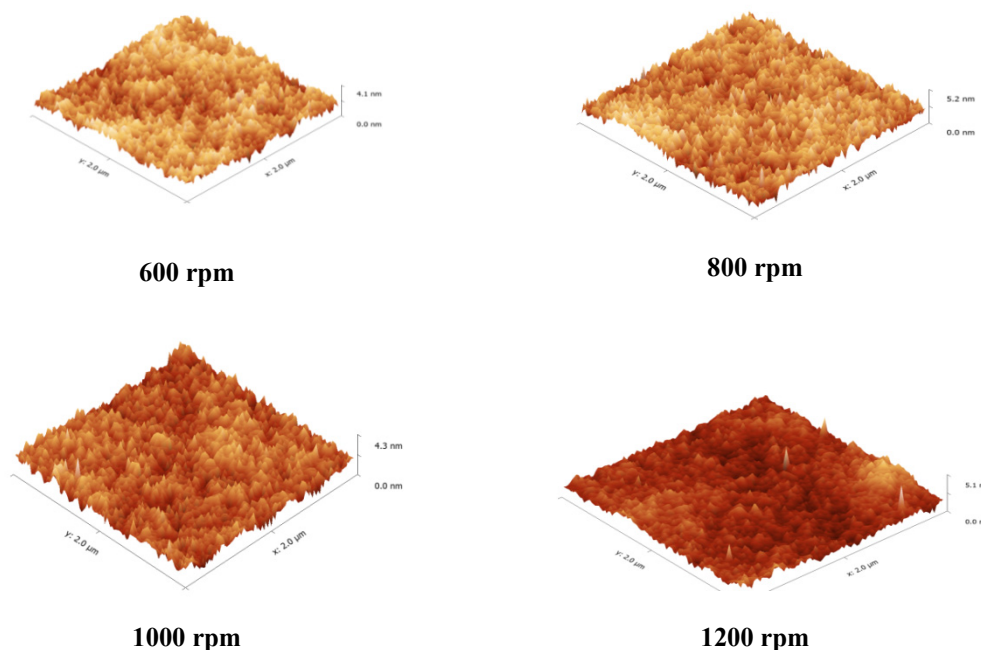

Figure 1. AFM images of PMMA thin films coated at 600, 800, 1000, and 1200 rpm

Furthermore, in order to determine the PMMA thin films optical properties and films thicknesses, spectroscopic ellipsometric data were collected and analyzed. However, the big challenge in our study that we have a wide spectral range 380 nm to 750 nm at 2.5 nm increments which mean 149 different values for each Ψ and Δ. As mentioned previously, these values will be converted into refractive index (n), extinction coefficient (k) and thicknesses. Therefore, to overcome these obstacles, we have employed MSA approach on four samples of PMMA with four different thicknesses in order to reduce the unknown parameters. As mentioned before, all films have the same material with the same optical constants i.e. 149 for each n and k with only four thicknesses. Therefore, a model was built for one sample consisting of various layers starting from silicon substrate with thickness of 1 mm, covered by a layer of silicon oxide with thickness of 30Å, and a layer which was used as an initial estimate for the optical constants of PMMA. Figure 2 shows the model structure and the thicknesses determined by WVASE software calculations.

Figure 2. An initial optical model structure for PMMA thin film

The refractive index (n) of PMMA transparent glass like layer was calculated using Cauchy dispersion model (Guide to Using WVASE 32®: Software, 2009) given by:

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

Where λ is the wavelength, and A, B and C are the Cauchy dispersion model constants. This layer exists in WVASE library as CAUCHY.MAT file. Upon choosing 1.54 as an initial estimate for A, 0.01 for B, and zero for C, we performed the simulation on thickness only and the result was the initial estimate of the PMMA thickness which was about 4023 Å with MSE of 35. The second step was performing a fit on thickness with parameter A, the MSE became 27. Next doing a fit on thickness, with A, and B parameters, the MSE came out 18. Finally performing a fit on thickness with all three parameters (A, B, and C) the resulted MSE value of about 12, for more details on this step, refer to Table 1.

Table 1. Summary of results on film thickness and model parameters of PMMA thin film

MSE	8.3
PMMA thickness	402.372±1.34 nm
A	1.56405±0.000624
B	0.0041302±2.45e-005
C	0.0001349±4.07e-006

In order to obtain more precise values of thicknesses, we have made an assumption that the layers are bounded by parallel plane interfaces. Whereas, WVASE software allows adding a layer called "roughness" which simply means a deviation from planarity. This roughness layer were added to our model (refer to Figure 3) then the simulation were performed using effective medium approximation (EMA) theory (Webman et al., 1977). Eventually this approximation will improve MSE to a more acceptable value of about 8. Just to mention that, this approximation uses a 50:50 mixture of the material and voids at the sample surface to get optical constants that estimates the surface roughness effect. Moreover, with this final model we are able to adjust the optical constants function to better describe the material. While Figure 4 represents the generated and experimental values of Ψ and Δ over the wavelength range 380-750 nm, Figure 5 represents the refractive index and extinction coefficient of PMMA thin layer, these observations are consistent with previously published works (Jimenez et al., 2012; Taqatqa & Al Attar, 2007; El-Nasser & Ali, 2010).

3	srough	15 Å
2	PMMA_Initial	4012.1 Å
1	SiO$_2$	30 Å
0	Si	1mm

Figure 3. A modified optical model structure for PMMA thin film after inserting a roughness layer
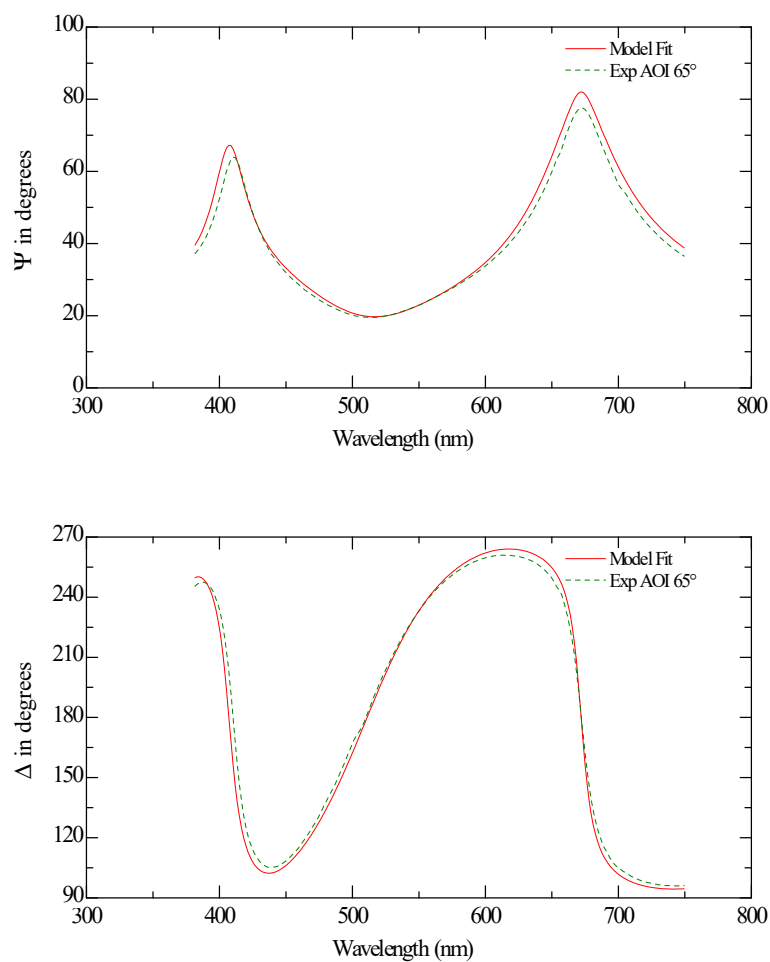
Figure 4. The optical constants Ψ and Δ for PMMA (600 rpm) thin film modulated as a Cauchy dispersion relation
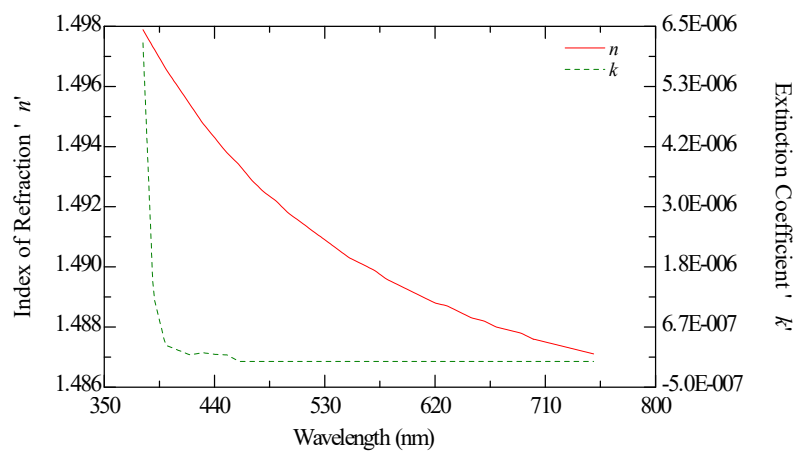

Figure 5. The index of refraction and extinction coefficient for PMMA thin film modulated as a Cauchy dispersion relation

The above model was not used only to calculate the refractive index and extinction coefficient of PMMA thin layer, but also it was used to increase the accuracy of the estimated films thicknesses. Therefore, we have used it as a preliminary characterization for the other three PMMA samples. This has been achieved by providing inputs to the subsequent detailed MSA based on SE. Then, a four layer model was employed to represent PMMA thin films deposited on silicon substrates. After that, fitting was performed simultaneously using MSA feature that couples optical properties across all four samples, assuming that the optical constants for all samples are identical, while the films thicknesses were allowed to be as fit parameters. Table 2 lists the MSA information from fitting window in WVASE software.

Table 2. Summary of results on film thicknesses and model parameters of PMMA thin films

MSE	11.2
PMMA_600 thickness	406.274±0.125 nm
PMMA_800 thickness	381.015±0.102 nm
PMMA_1000 thickness	353.468±0.433 nm
PMMA_1200 thickness	326.025±0.285 nm
A	1.5047±0.000354
B	0.00328±1.25e-005
C	0.000214±7.07e-006

4. Conclusions

In summary, the morphology, optical constants, and the thicknesses of PMMA thin films were studied using AFM and spectroscopic ellipsometry. Although, A Cauchy dispersion relation model was adapted to obtain optical properties for PMMA thin films. It was found that spectroscopic ellipsometry data are extremely sensitive to the material optical constants. Furthermore, an employment of a multiple sample analysis will reduce model parameter correlations and errors. This allows determining the films thicknesses precisely. Therefore, understanding such materials has a direct impact on the studying devices properties in which they may be implemented.

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