Effect of Molecular Weight and UV Illumination on Optical Constants of PMMA Thin Films

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Received 1 September 2009; accepted 12 December 2009

ABSTRACT

The refractive index of poly(methyl methacrylate) (PMMA) thin films on glass substrates, prepared by spin coating method has been studied using a spectroscopic ellipsometry. Spectroscopic ellipsometry measurements of PMMA thin films were carried out at three angles of incidence, over the wavelength range of 400-700 nm. Optical Cauchy model was used to obtain thickness of the prepared films along with some optical constants. Each PMMA thin film shows a characteristic dispersion relation, although they all behave similarly. Refractive indices were found to be in the range 1.49-1.53 with the maximum wavelength at 400 nm, and found to increase with increasing molecular weight of PMMA, and consequently causing an increase in film thickness. It was found that changing the molecular weight of PMMA and as a result the thickness of the films prepared made significant changes in both real (\(\varepsilon_1\)) and imaginary (\(\varepsilon_2\)) parts of the dielectric constant as a function of wavelength. The \(\varepsilon_1\) and \(\varepsilon_2\) peaks near 570 and 500 nm, respectively, were shifted towards lower energy upon increasing molecular weight. The refractive index variation and the appearance of surface roughness after UV illumination were evident. The roughness is modelled after fitting the spectroscopic ellipsometry data by using Bruggeman effective medium approximation assuming 50% PMMA and 50% voids. It was found that the UV illumination for one hour decreases the refractive index by 2 x 10^{-3}. The refractive index changes upon UV illumination might be attributed to different factors namely: (i) microstructural defects; (ii) decomposition of PMMA molecules; (iii) carbon-oxygen polarization; and (iv) dipole-dipole intermolecular interactions.

INTRODUCTION

Polymer materials have been widely used in various fields such as industrial products, optical communications [1], including polymer optical fibres, optical waveguides and optical connectors due to their ease of processing, relatively low cost and mass production compared to silica based optical materials. They also have potential advantages for applications in optical storage systems [2], such as high thermal stability, low absorption loss and the ability of refractive index changing upon exposure to light. Polymer-based optical devices have attracted great interest in the low loss optical communication systems and optical switches with
low driving power [3].

Poly(methyl methacrylate) (PMMA) has drawn tremendous interest due to its optical properties and its possible use in non-linear optics. Optical properties of PMMA depend on its molecular structure and could be modified by several methods such as external electric field and UV illumination [4-7].

Recently, Park et al. [8] have investigated the polymerization kinetics of methacryl groups and refractive index changes by ultraviolet illumination. Current interests of many researchers focus on the effect of UV illumination on PMMA thin films, which leads to a photo-degradation, photo-cross-linking, photochemical reactions, depolarization, random chain scission, side group abstraction and oxidation [9].

Spectroscopic ellipsometry has been used to study optical and structural properties in polymer thin films at atmospheric conditions [10-12], glass transition temperatures and adsorption of surfactants [13]. In spectroscopic ellipsometry, the change in polarization state of light reflected from a film is measured to determine both the thickness and refractive index of the thin film. The ellipsometric data were acquired over a broad spectral range at several angles of incidence. An optical model representing the assumed physical geometry and microstructure is used, and Fresnel reflection coefficients are calculated, allowing predictions of ellipsometric data to compare with measured values. Model parameters, such as refractive index, n, extinction coefficient, k, and thickness, vary in regression until the comparator function, such as the mean square error is minimized. The resulting parameters are the "best-fit" values of n and k. Spectroscopic ellipsometry determines two angles \( \Psi \) and \( \Delta \) according to eqns (1) and (2):

\[
\tan \Psi = \left| \frac{r_p}{r_s} \right| \quad \text{(1)}
\]

\[
r_p/r_s = \exp(i\Delta) \tan \Psi \quad \text{(2)}
\]

where \( r_p \) and \( r_s \) are the complex Fresnel reflection coefficients for 'p' and 's' polarizations, respectively, and \( \Delta \) is a phase shift between both polarized waves. Both angles in the equations allow determination of the thickness of a film and the spectral dependencies of optical constants (refractive index and extinction coefficient). Ellipsometric measurements permit also determination of the roughness of the layer surface. Since \( \Psi \) and \( \Delta \) values can only be converted to the studied parameters (refractive index, extinction coefficient, film thickness, etc.) of the sample, usually a fitting procedure is used for their determination. First a model is built where the structure of the sample and some optical properties are assumed, whereupon, \( \Psi \) and \( \Delta \) values are generated. Then the model is changed by a fitting algorithm in order to minimize the difference between the generated and measured data. The difference is measured with the mean square error (MSE), using eqn (3):

\[
MSE = \left[ \frac{1}{2N-P} \sum_{i=1}^{N} \left( \left( \frac{\Psi_i - \Psi_{i}^m}{\sigma_{\Psi_i}} \right)^2 + \left( \frac{\Delta_i - \Delta_{i}^m}{\sigma_{\Delta_i}} \right)^2 \right) \right]^{1/2}
\]

where \( \Psi_i \) and \( \Delta_i \) represent the measured \( \Psi \) and \( \Delta \) angles at the ith wavelength; \( \delta \) is the standard deviation; upper indices m and g denote the measured and generated data, respectively; while N and P represent the number of measured values and fitted parameters, respectively.

In the present work, we report the effect of molecular weight and thickness on some important optical parameters such as refractive index and dielectric constant of PMMA thin films deposited onto glass substrates using variable angle spectroscopic ellipsometry. Also UV illumination effect on PMMA thin films was studied to evaluate the refractive index along with surface changes. The results provide promising information on PMMA based devices which are important for academic as well as industrial applications.

**EXPERIMENTAL**

**Materials**

An amount of 0.1 g of each grade of poly(methyl methacrylate) (PMMA) purchased from Fluka-Aldrich, with linear formula \([-\text{CH}_2\text{C(CH}_3\text{)}\text{(CO}_2\text{CH}_3\text{)}\text{]}_n\) and GPC measured molecular weights 15000, 300000, 996000, was dissolved separately in 20 mL chlorobenzene of purity 99%. The solutions were then filtered using 0.5 μm filters to remove any
non-dissolved impurities and dust before use. Before film preparation, microscope glass slides as substrates were dipped in a saturated potassium dichromate solution in concentrated sulphuric acid, and then rinsed thoroughly with portions of distilled water followed with acetone. A set of three PMMA thin films on glass substrates were obtained using the spin coating method with a spinning time of 20 s and a spin frequency of 1500 rpm. All samples were prepared at room temperature and left to dry for 24 h.

To investigate the UV effect, the samples were illuminated using UV lamp (250 μW/cm²) filtered at λ = 254 nm at different illumination times. Ellipsometric measurements were carried out using a variable angle spectroscopic ellipsometer (VASE™) of the rotating analyzer type. The measured quantities are known as the ellipsometric parameters Ψ and Δ, which are indirectly related to the optical and structural properties of the sample. All measurements were performed in air at room temperature for three angles of incidence 65, 70 and 75 degrees in the range of 400-700 nm (steps of 10 nm). The acquired data were simultaneously analyzed using WVASE32® software to determine the refractive index and the eventual thickness of the films.

RESULTS AND DISCUSSION

A glass was used as a substrate for thin films in this work. Its transparency in the visible range, and internal reflections, are of concern for ellipsometry. Since the light penetration depth is high, reflection from backside of a glass slide can be only suppressed either by abrading and/or blackening the backside surface, or by using a suitable analysis software, which includes contributions of a second light beam (two reflected beams reach the detector from the top and back glass surfaces) [17,18]. In this work abrading and blackening the backside surface are being used to achieve this suppression. The glass substrate optical constants were measured in the same conditions prior to analysis of the films. The refractive index of the substrate was saved and the extinction coefficient was kept zero [19].

To determine dispersion refractive index of PMMA layers a Cauchy dispersion model was used to analyze the spectroscopic ellipsometry data [20] in order to determine n:

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

where λ is the wavelength, while A, B and C are Cauchy dispersion model constants.

This model structure was used to fit the spectroscopic ellipsometry data taken on all samples of PMMA thin films (A1-A3 samples). The best-fit model parameters for PMMA samples are presented in Table 1 showing the thickness and Cauchy parameters of PMMA films. We observe that the values of the same parameter for all samples are close together, which indicate the validity of the model adopted for the films.

Figure 1 shows spectrum of PMMA (sample A1) film deposited by spin coating on glass substrate. There are two characteristics of the experimental data shown in this figure. The first one is related to the fact that the system is transparent at wavelengths 400-700 nm, the second feature is its weak dependency on the angle of incidence.

The dispersion refractive index curves obtained from ellipsometry for three molecular weights of PMMA are presented in Figure 2. The three curves are clearly different, but obviously show a similar behaviour. Refractive indices of PMMA thin films

Table 1. Thin film samples: film thickness, and parameters of Cauchy model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PMMA molecular weight (GPC)</th>
<th>Film thickness (nm)</th>
<th>Cauchy parameters</th>
<th>Mean square error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A (nm)</td>
<td>B (nm²)</td>
</tr>
<tr>
<td>A1</td>
<td>15000</td>
<td>518 ± 7%</td>
<td>1.5 ± 0.5%</td>
<td>0.018 ± 2.8%</td>
</tr>
<tr>
<td>A2</td>
<td>300000</td>
<td>621.68 ± 9%</td>
<td>1.49 ± 0.3%</td>
<td>0.031 ± 3.4%</td>
</tr>
<tr>
<td>A3</td>
<td>996000</td>
<td>814 ± 6%</td>
<td>1.5 ± 0.32%</td>
<td>0.025 ± 4.6%</td>
</tr>
</tbody>
</table>
Figure 1. Spectroscopic ellipsometric parameter versus wavelength of PMMA (sample A1) thin film on glass substrate. The triangle, square, and circle lines represent the experimental data while the solid line is the model fit for angles of incidence 65º, 70º and 75º. weres found to be in the range of 1.49 and 1.53 with the maximum wavelength at 400 nm. Variation in refractive index follows the normal dispersion law, and the estimated values of refractive index are close to the reported values [21]. It is interesting to note that the refractive index is related to the molecular weight. By comparing dispersion relations given in Figure 2, it is evident that refractive index increases with increasing molecular weight, which leads to increases in film thickness, and the refractive indices of the film with 518 nm thickness (A1 sample) are less than those of films with thicknesses of 621 and 814 nm. This observation is consistent with other results [22-25]. The similar behaviour in the dispersion curves indicates that the three films are of the same material but different densities.

Figure 2. Refractive index of PMMA thin films of three values of molecular weight.

Figure 3. The variation of real and imaginary parts of the dielectric constant with wavelength: (a) real part and (b) imaginary part.

The real and imaginary parts of dielectric constants $\varepsilon_1$ and $\varepsilon_2$ as a function of wavelength of A1-A3 samples are shown in Figures 3a and 3b. The complex dielectric function is given by:

$$\hat{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$  \hspace{1cm} (5)

$$\varepsilon_1 = n^2 - k^2$$  \hspace{1cm} (6)

$$\varepsilon_2 = 2nk$$  \hspace{1cm} (7)

As shown in these figures the curves of $\varepsilon_1$ and $\varepsilon_2$ reveal that the general behaviour of these constants is the same and shows maximum value near the absorption edge. From Figure 3a it may be observed that the variation of $\varepsilon_1$ with wavelength shows that
the peak value near 570 nm is shifted towards lower wavelength with increased molecular weight, while Figure 3b shows that the peak value near 500 nm is also shifted towards lower wavelength. It is concluded that the values of $\varepsilon_1$ are higher than values of $\varepsilon_2$ because $\varepsilon_1$ mainly depends on $n^2$. The molecular weight of PMMA and accordingly the thickness of the films cause significant changes in real and imaginary parts of the dielectric constant.

Ellipsometry measurements were performed also for PMMA/glass systems after UV illumination, and fitted the data with the above described fitting model, but some changes were made by assumptions on the appearance of the surface roughness, which can be described using the Bruggeman effective medium approximation [26]. This approximation uses a 50:50 mixture of the material and voids at the sample surface to obtain optical constants that approximate the effect of the surface roughness. The effect of UV illumination time of PMMA thin films at two wavelengths 635 and 470 nm on the refractive index was found to be significant as shown in Figures 4 and 5. It is noteworthy that the samples need one hour of UV illumination to decrease the refractive index by $\sim 2 \times 10^{-3}$. These changes in the refractive index values may be attributed mainly to different contributions due to:

- Microstructural defects, non-transparent glass substrate for UV illumination, an incident photon, which is probably not being absorbed by PMMA layer and it is reflected from the glass substrate surface, whereas its dissipation may cause absorption by polymer defects and initiation of cross-linkages, and the degradation of the polymer molecules and creation of oxidized groups in PMMA [27-31]. It is well known that photo-oxidative degradation is a free radical chain process and after its initiation on the polymer surface, the efficiency of degradation inside film depends on the diffusion and migration of radicals, oxygen and other reactive species. These processes are facilitated by the surface defects, small cracks and micropores.

- The decomposition of PMMA molecules upon UV illumination can be due to the influence of deeper polymer layers on surface macromolecules.

- Carbon-oxygen polarization as PMMA and glass substrate contain electronegative oxygen atoms, thus C-O bonds are polarized, resulting in specific interactions occurring at the interphase [32].

- Dipole-dipole nature, which leads to rearrangement of polymeric chains and bringing about the photochemical processes at PMMA surface.

CONCLUSION

The refractive index behaviour of PMMA thin films was studied using spectroscopic ellipsometry, which covers a visible spectral range. This technique can detect small changes in optical constants. The
thickness effect of PMMA films on the refractive index was obtained. Films of different molecular weights exhibited different thicknesses and accordingly different dispersion relations, but the behaviour of these relations was the same. UV illumination of PMMA thin films enhanced the decomposition and degradation of PMMA molecules that contributes to the refractive index change, and initiating a surface roughness depending on the UV illumination time.

ACKNOWLEDGEMENT

The authors are grateful to Deanship of Graduate Studies at Al al-Bayt University for the support.

REFERENCES


