Spectroscopic Ellipsometry of Azo Dye Doped Polymer Thin Films

Husam El-Nasser, Taha Khudur and Basem Ali*

ABSTRACT

The optical constants of azo dye (Methyl Red MR) and azo dye doped polymer (Poly Methyl Meth Acrylate PMMA) at various values of acidity (pH) have been investigated using Variable Angle Spectroscopic Ellipsometry (VASE). The acidity of the MR has been varied to study the changes in the refractive index of the mixture. It was found that the refractive index increases with increasing the pH of MR solution. Pure MR and constituents MR/PMMA were modeled using the mathematical models of Lorentz and Bruggemann effective medium approximation. Ellipsometric data were taken over the spectral range 300-1000 nm at different angles of incidence.

Results show that these materials can be considered as alternative optical substances with better storage properties.

KEYWORDS: Spectroscopic ellipsometry, Refractive index, Extinction coefficient, Azo dye, Polymethylmethacrylate.

1. INTRODUCTION

Polymeric optical materials are of great interest for applications in optical communications, including polymer optical fibers, optical waveguides and optical connectors due to their ease of processing, relatively low cost and mass production compared to silica based optical materials (Prasad, Williams, 1991). Polymeric optical materials have also potential advantages concerning some properties, such as high thermal stability and low absorption loss at the optical wavelength 1-3 µm (Pham et al., 1995; Hilfiker et al., 1998). High performance in the infrared region is systematically important in devices for optical applications (Yoshimura et al., 1998). Optical storage media has become a core technology in the multimedia environment for both entertainment and computing industries (Min et al., 1999). Rapidly increased information solicits a more convenient and efficient storage method (Suzuki et al., 1999). The structure of an optical data storage system consists of polycarbonate (PC) substrate, a recording layer, a metal reflective layer, and a protective layer (Park et al., 2002). The recording layer is easily decomposed by laser light with particular wavelengths (Sugiyama, Neubert, 1997). The recording layer has a high refractive index, so it can effectively absorb light and generate heat when the laser beam is focused on the film. The heat is transferred to both the PC substrate and the recording layer. In order to achieve a better storage medium, some factors should be considered: a high refractive index at 635nm which is most generally used in DVD players, thermal stability at high temperature, and a good solubility for a spin coating process onto substrate.

In this work, spectroscopic ellipsometry was used to study and characterize the changes in the optical constants in thin films composed of azo dye doped polymer with several acidity values.

The ellipsometric data $\Psi$ and $\Delta$ are acquired over a broad spectral range at several angles of incidence (Woollam et al., 2003). In each spectral range, different properties of materials are obtained. However, the data must be analyzed to obtain useful information. An optical model representing the assumed physical geometry and microstructure is developed, and Fresnel reflection coefficients are calculated, allowing predictions of $\Psi$ and $\Delta$ to compare with measured values. Model parameters, such as refractive index n, extinction coefficient k, and thickness, vary in regression until the
Table (1): Thin film samples with their volume ratio and acidity pH.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>MR:PMMA volume ratio</th>
<th>Acidity,pH</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1:0</td>
<td>4.54</td>
</tr>
<tr>
<td>2</td>
<td>0:1</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
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<td>1:3</td>
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<tr>
<td>9</td>
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<td>11</td>
</tr>
</tbody>
</table>

Fig.(1): Ellipsometric parameter $\Psi$ of normal MR (pH=4.54).

2. EXPERIMENT

Methyl Red (MR) and Poly Methyl Meth Acrylate (PMMA) were dissolved separately in chlorobenzene and ethanol of purity 99%. Different acidity degrees were obtained by adding NaOH, HCl, and paradine. Samples No 1 and 6 were prepared without any addition because the normal pH for these samples is 4.54. Mixture solutions of MR and PMMA were achieved with volume ratio 1:3. Table (1) shows the prepared samples, their MR: PMMA volume ratio and pH value. Sample No. 3 (pH=0) was used as an indication of the very high acidity of the solution. The solutions were then filtered using 0.5 $\mu$m Millipore filter to remove any dissolved impurities and dust before use. All samples were prepared at room temperature and left to dry 24 hours. A set of thin films was obtained of individual and mixture media using the spin casting method on glass substrates.

Ellipsometric data were acquired with a variable angle spectroscopic ellipsometry (VASE™, J.A.Woollam Co.) of the rotating analyzer type. All measurements were performed in the air at room temperature for three angles of incidence 65°, 70°, and 75° in the wavelength range of 300-1000 nm in steps of 5 nm.
Fig. (2): Optical constants: refractive index and extinction coefficient of normal MR (pH=4.54).

Fig.(3): The refractive index for MR thin films of several pH values at 635 nm.
3. RESULTS AND DISCUSSION

A. Methyl Red (MR)

We have adopted the result (Hameed, Osama, 2003) that three oscillators of Lorentz model centered about 2.5, 2.1 and 4 eV give a satisfactory description for the optical constants for MR. Fig. (1) shows the ellipsometric $\Psi$ and Fig.(2) shows the optical constants $n$, $k$ of MR thin film (sample No 6). Measurements of refractive index were carried out at various pH values (0-11 range), keeping other parameters constant. The acidity effect (expressed as pH) on the refractive index can be deduced from Fig.(3). It can be seen that the refractive index at $\lambda = 635$ nm, increases by increasing the pH, and reaches a value (> 2), which in turn improved the goodness of the storage medium properties (Park et al., 2002). This trend might be attributed to the resulting basic form of methyl red Fig.(4). This form represents more charge delocalization on the molecule and in turn more polarizability that allows for larger aggregation of molecules as a result of stronger intermolecular interactions. Accordingly, the acidity could be considered as an important factor that affects and improves some spectroscopic optical constants such as the refractive index.
Fig.(6): Ellipsometric parameter $\Psi$ of mixture MR/PMMA (pH=4.54).

Fig.(7): Optical constants: refractive index and extinction coefficient of mixture MR/PMMA (pH=4.54).
B. Polymethylmethacrylate (PMMA)

PMMA is used to support the film because of its good optical and mechanical properties (Pham et al., 1995). Spectroscopic ellipsometry measurements for a blank glass substrate, and PMMA on glass substrates were analyzed by fitting the $\Psi$ and $\Delta$ data, using the Cauchy formula:

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

where A, B, and C are the Cauchy parameters (James et al., 1998). Since PMMA is transparent in the visible and Near Infrared Region (NIR), the refractive index must decrease with increasing wavelength as shown in Fig.(5). The extinction coefficient, which describes the absorptive properties of PMMA to light of a given wavelength, is near zero. Therefore, visible and NIR light transmits through PMMA without energy loss.

C. MR/PMMA:

The optical constants of thin films MR/PMMA were determined using the Bruggemann Effective Medium Approximation (EMA) given by:

$$f_A \tilde{\varepsilon}_A + f_B \tilde{\varepsilon}_B + f_C \tilde{\varepsilon}_C = 0$$

where $f_A$, $f_B$, and $f_C$ are the volume fraction of the constitutions (Azzam, Bashara, 1987). In this model, the film is regarded as composed of three components. Isolating the part of one component of complex dielectric constant $\tilde{\varepsilon}_A$, the rest of the film is regarded as a homogeneous medium of complex dielectric constant $\tilde{\varepsilon}$.

The chosen part is assumed to be spherical in shape. The calculation is then repeated with respect to the other components B and C etc. The complex dielectric function can then be expressed as a real and imaginary part:

$$\tilde{\varepsilon} = \varepsilon' + i \varepsilon''$$

The refractive index (n) and the extinction coefficient (k) are related to $\varepsilon'$ and $\varepsilon''$ by:

$$\varepsilon' = n^2 - k^2$$

$$\varepsilon'' = 2nk$$

Fig.(6) shows the ellipsometric parameter $\Psi$ of MR/PMMA system at pH=4.54. There are two characteristics of the experimental data shown in this figure. The first one is related to the fact that the MR/PMMA system is nearly non-absorbing at wavelengths greater than~600 nm, while the second
feature is the lack of dependence on the angle of incidence. Fig.(7) shows that the refractive index and the extinction coefficient follow that of the MR graph, although the absolute value of the refractive index is low in comparison with that of the individual constituent MR Fig.(8). This difference may be attributed to their volume contribution. The maximum value of refractive index occurs at 577nm for MR, and at 420nm for the MR/PMMA films.

4. CONCLUSION

Spectroscopic ellipsometry is a very powerful technique for optical characterization of thin films. It covers a wide spectral range and it can detect small changes in optical constants. The percent error and the goodness of data in measurements were determined by the Mean Square Error (MSE). The value of MSE, which represents the quality of the model used for fitting process, is defined according to the WVASE32 software. Accordingly, MSE values that are less than 10 are acceptable and represent a good fit. In our case, all MSE values are in the range $2 < \text{MSE} < 8$, and therefore are considered as acceptable.

We have investigated the optical constants of azo dye doped polymer (MR/PMMA) systems by characterizing each material individually, and then constructing a model to characterize the system as a whole. MR thin films exhibit an increase in refractive index at 635nm when increasing its pH value. It is shown that doping azo dye in PMMA thin films is of promising potential for optical storage media.

REFERENCES


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(PMMA) and (MR) study of the color development of the red paint (MR) and polystyrene (PMMA) layers using the 

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