

In situ measurement of humidity induced changes in the refractive index and thickness of polyethylene glycol thin films

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ABSTRACT

Humidity induced changes in the refractive index and thickness of polyethylene glycol (PEG) thin films are *in situ* determined by optical waveguide spectroscopy. PEG brushes are covalently attached to the surface of a thin gold film on a borosilicate crown glass (BK7) using a grafting-from chemical synthesis technique. The measurements are carried out in an attenuated total internal reflection setup. At low humidity levels, both the refractive index and the thickness change gradually due to swelling of the PEG thin films upon water intake. At around 80% relative humidity, a steep decrease in the refractive index and a steep increase in the thickness are observed as a result of a phase change from a semicrystalline state to a physical gel state. The hydrogenation of PEG films causes a less pronounced phase change from a semicrystalline state to a gel state. Due to fewer ether oxygen atoms available for the water molecules to make hydrogen bonding, the polymer has a more stable structure than before and the phase change is observed to shift to higher humidity levels. It is discussed that such a humidity induced change in the index of refraction can be utilized in constructing of a PEG based humidity sensor.

Keywords: humidity sensor, polyethylene glycol, optical waveguide spectroscopy

1. INTRODUCTION

In situ humidity induced changes in the index of refraction and thickness of PEG layers are determined using an experimental attenuated total internal reflection procedure, which is based on surface plasmon resonance (SPR) [1, 2] and optical waveguide spectroscopic [3, 4] methods. Surface plasmons are the electromagnetic waves that propagate along the metal-dielectric interface, which form the base of the surface plasmon resonance (SPR) spectroscopy. One way of forming an evanescent wave (and, hence, a surface plasmon) is to make use of the total internal reflection of a plane electromagnetic wave at the base of a glass prism in contact with an optically less dense medium, preferably with a metal layer evaporated onto the base of the prism. To determine the refractive index and the thickness of PEG films, the polymer should be deposited on a thin metal layer and should have a certain thickness and homogeneity to satisfy the optical waveguiding condition. An optical waveguide structure is a high refractive index medium sandwiched in a lower refractive index environment. A metal layer whose index of refraction is lower than the waveguide on one side of the polymer film and air on the other side satisfy this condition. Gold, which is a chemically inert metal, is evaporated on a BK7 glass to introduce surface plasmons. Growth of a stable PEG film onto gold is only possible by covalent attachment of the polymer molecules to the gold surface in concern. A chemical synthesis procedure called the grafting-from technique [5, 6] is used to prepare relatively thick PEG layers for our optical experiments.

The swelling behaviour of PEG layers in contact with humid air for the range 13% to 95% relative humidity is *in situ* studied. Experimentally measured refractive index and thickness values of the films are checked with theory, using Fresnel's equations [1, 7]. Much to our surprise, it is experimentally observed that a steep decrease in the refractive index and a steep increase in the thickness of PEG films occur at a humidity level of around 80%, as a result of a phase change from a semi-crystalline to a physical gel state. Afterwards, the films are hydrogenated and a less pronounced change in the refractive index and thickness is observed. The polymer is observed to be more stable than before.

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2. THEORY

Surface plasmon resonance and optical waveguide spectroscopy measurements are carried out to determine the refractive index and thickness of gold and PEG films. Such optical and physical parameters of both gold and PEG films are calculated from experimental reflection spectra, using an optical setup shown in Fig. 1. Experimental results on reflection spectra from a thin film assembly are observed to match with the theoretical curves obtained from Fresnel's equation. The reflection of light as a function of the incident angle θ for a p-polarized monochromatic light beam of wavelength λ , for a four-layer system, is given by [7]

$$R(\theta) = |r_{1,4}(\theta)|^2 \quad (1)$$

$$r_{t,4}(\theta) = \frac{r_{t,t+1}(\theta) + r_{t+1,4}(\theta) \exp(2iW_{t+1}k_{zt+1}(\theta))}{1 + r_{t,t+1}(\theta)r_{t+1,4}(\theta) \exp(2iW_{t+1}k_{zt+1}(\theta))} \quad (2)$$

where $t=1, 2$ and $i=(-1)^{t/2}$ and

$$r_{t,t+1}(\theta) = \frac{\zeta_{t+1}(\theta) - \zeta_t(\theta)}{\zeta_{t+1}(\theta) + \zeta_t(\theta)} \quad (t=1,2,3) \quad (3)$$

$$k_{zt}(\theta) = \frac{\omega}{c} \sqrt{\varepsilon_t - (\sqrt{\varepsilon_1} \sin \theta)^2} \quad (4)$$

$$\zeta_t(\theta) = \frac{\varepsilon_t}{k_{zt}(\theta)} \quad (t=1,2,3,4) \quad (5)$$

where ω and c are the angular frequency and the velocity of light in vacuum, respectively, k_{zt} is the wavevector component perpendicular to the interface in medium t ($t=1, 2, 3$ or 4), $r_{t,t+1}$ represents the reflection ratio for the $t - (t+1)$ interface, ε_t ($t=1, 2, 3$ or 4) is the dielectric constant of the media, W_t ($t=2$ or 3) represents the thickness of the gold and PEG film.

The index of refraction and thickness of the PEG film, represented by n_3 and W_3 respectively, are determined from the following equations [3]:

$$kW_3(n_3^2 - N_m^2)^{1/2} = \psi_m(n_3, N_m) \quad (6)$$

where

$$N_m = \sin \alpha_m \cos \delta + (n_1^2 - \sin^2 \alpha_m)^{1/2} \sin \delta \quad (7)$$

and

$$\psi_m(n_3, N_m) = m\pi + \Omega_2(n_3, N_m) + \Omega_4(n_3, N_m) \quad (8)$$

$$\Omega_j(n_3, N_m) = \arctan \left[\left(\frac{n_3}{n_j} \right)^{2\rho} \left(\frac{N_m^2 - n_j^2}{n_3^2 - N_m^2} \right) \right]^{1/2} \quad (9)$$

with $j=2, 4$. δ is the prism angle and ρ is the polarization state of the laser beam ($\rho=0$ for s-polarization and $\rho=1$ for p-polarization). Inserting Eq. (7) into Eq. (6) and Eq. (8)-(9) yields unique solutions of n_3 and W_3 for two modes. In case of observing only one mode, one of the unknowns can still be determined if the other is known from another measurement. For more than two mode numbers the unknowns are over determined.

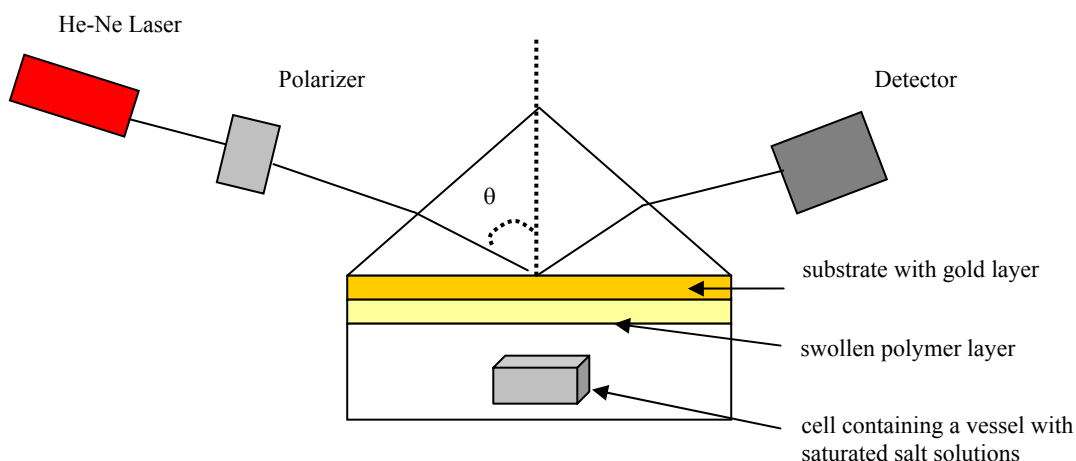


Fig. 1. Optical setup.

3. EXPERIMENT

3.1 Sample preparation

Grafting-from chemical synthesis technique [5, 6] is used to deposit PEG films about 1 μm thick on the surface of gold thin films - coated on BK7 glass slides. An approximately 50 nm thick gold layer is evaporated onto the slides prior to polymer coating. Grafting-from technique is utilized to synthesize dense polymer brushes that can show response to humidity. After polymerization reaction, the samples are gently rinsed with ethanol to remove any loosely physisorbed polymer. Ethanol is used since it is a good solvent for the polymer. Samples are left under vacuum overnight to be sure that all ethanol is removed from the surface. Thus, obtained dense polymer brushes with high affinity for moisture are probed for utilization as humidity sensors.

3.2 Optical setup

An optical waveguide spectroscopic setup (or, the Kretschmann [8] configuration of the attenuated total internal reflection method) shown in Fig. 1 is employed to in situ determine the humidity induced changes in the index of refraction and thickness of a thin PEG polymer film. A p-polarized monochromatic light of wavelength 632.8 nm from a helium-neon (He-Ne) laser is employed as the monitoring beam. As shown in Fig.1, the p-polarized light is coupled into the PEG film through a glass prism and a ~ 50 nm thick gold thin film. The glass prism is made of BK7 material with a refractive index of 1.5151. At the stage of sample preparation, the gold and PEG films are initially deposited on a half-cm thick separate BK7 glass. The other empty side of this gold-PEG coated BK7 glass is brought into contact with the BK7 prism. By not coating gold and PEG films directly onto the base of the BK7 prism, we aimed to save the prism for multiple uses in our experiments. An index matching oil of 1.5167 (Cargille Laboratories Inc. NJ) is inserted between the glass prism and coated BK7 glass in order to avoid unwanted reflections from discontinuous interfaces.

During angular scans, the reflected intensity $R(\theta)$ is detected by a large area silicon detector as a function of incidence angle θ (see Fig. 2). Experimental spectra curves on reflection are fitted with theory on $R(\theta)$, which is given by Eq.(1). Refractive indices and thicknesses of gold and PEG films are calculated from these reflection spectra using the theoretical procedure given in the previous section. The same optical setup is used to in situ determine the swelling kinetics and the humidity induced changes in the refractive index and film thickness. As shown in Fig. 1, the sample is brought into contact with a cell, which is held at a constant temperature and a constant humidity level. A vessel with saturated salt solutions [9] is inserted into the cell to control the humidity inside. The high salt content of the solution reduces the vapour pressure of the water to a distinct value. During moisture exposure the change in optical and physical properties are monitored by measuring the shift in reflection spectra's minima of the waveguide modes. When a specific

humidity value is reached –without changing the temperature of the vicinity- the sample is scanned as a function of the incident angle from 30° to 90° to obtain reflection spectra shown in Fig. 2.

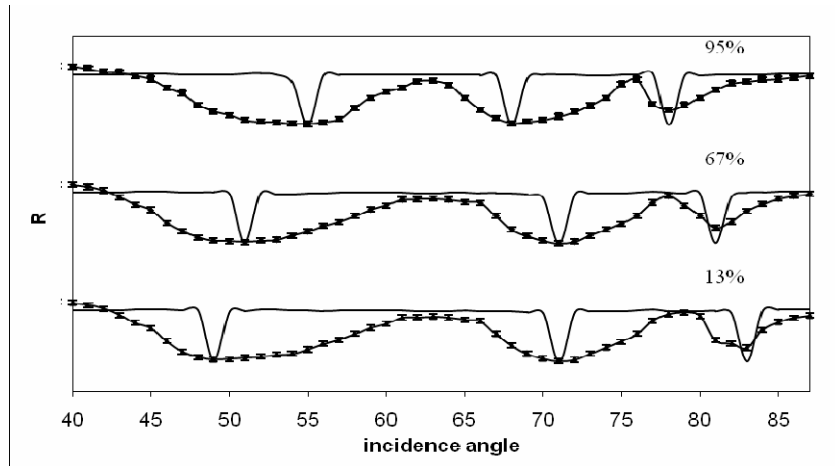


Fig. 2. Waveguide spectra measured at different constant relative humidities. The solid lines are the calculated reflection curves obtained from Eq. (1).

4. RESULTS

Optical waveguide spectroscopy experiments are performed for in situ determination of the refractive index and thickness of the PEG layer, which is coated on top of the gold sample. To investigate the swelling behaviour of PEG film in contact with humid air, we insert a small vessel containing saturated aqueous salt solutions. Dips in the reflectivity curves in Fig. 2 indicate the existence of several guided wave modes. For a given material, the number of the guided modes and their angular positions depend only on the waveguide thickness [4]. The angular positions of the waveguide modes allow us to determine the thickness and the refractive index of the PEG polymer single layer using waveguide Equations (6)-(9).

Reflection curves as a function of the angle of incidence (at 25 °C) at different constant relative humidity values are shown in Fig. 2. As can be seen in Fig. 2; with increasing humidity of the film’s environment, the higher order waveguide modes, which are located at the smaller angles of incidence, shift to bigger angles, indicating an increase of the film thickness and a change in the index of refraction due to diffusion of water into the polymer layer.

Fig 3 shows the in situ relative humidity induced change in the thickness of the PEG sample. It is clearly seen that as relative humidity of the environment increases the thickness of the polymer increases due to absorption of water and the consequent swelling of the polymer layer. Much to our surprise, an unexpected and distinctive swelling is observed in our experiments at a relative humidity around 80%, which is indication of a phase change from one physical state to another.

Fig. 4 shows in situ relative humidity induced change in the refractive index of the same PEG sample. At very low humidity levels, between 13% and 16%, there is a slight increase in the refractive index, from 1.4522 to 1.4549. For this particular relative humidity region, $dn_3/dH_R = +9.0 \times 10^{-4}$. As the water molecules start to diffuse into the PEG polymer layer, the refractive index begins to decrease from 1.4549 to 1.4298 for the relative humidity range from 16% to 76%, at a relatively moderate level corresponding to $dn_3/dH_R = -4.0 \times 10^{-4}$. As the humidity reaches around 80%, the refractive index of the PEG layer (n_3) undergoes an abrupt decrease in a similar manner to that observed in the physical thickness of the polymer film shown in Fig 3. n_3 decreases from 1.4298 to 1.4125 just for a small relative humidity range of about 3%, from 76% to 79%. This also confirms the phase change from one physical state to another. For this particular phase transition region $dn_3/dH_R = -5.8 \times 10^{-3}$.

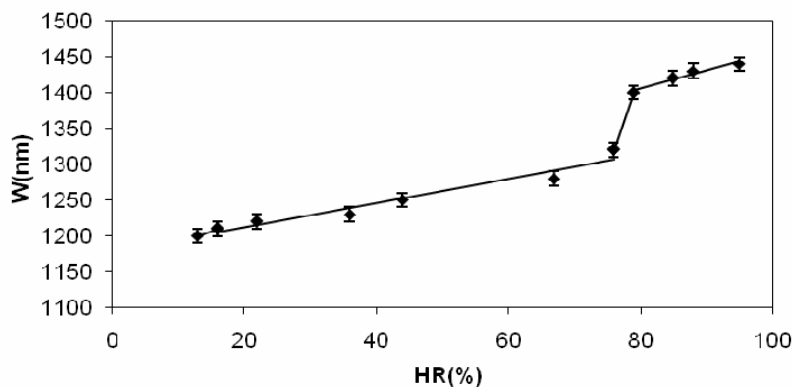


Fig. 3. Thickness of the PEG film as a function of relative humidity from 13% to 95%.

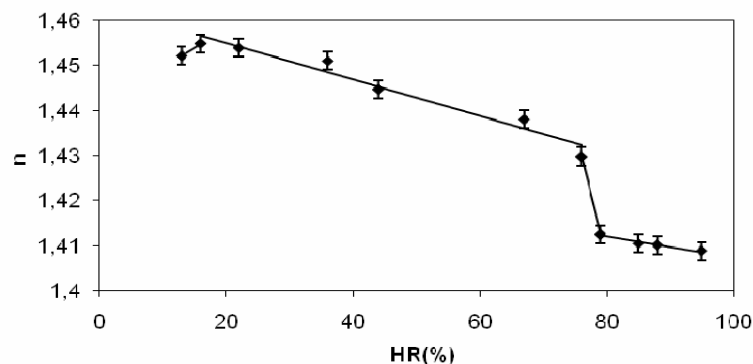


Fig. 4. Refractive index of the PEG film as a function of the relative humidity from 13% to 95%.

5. DISCUSSION

The phase transition at a relative humidity of around 80% causes an abrupt change in the refractive index and thickness of the polymer layer. Distinctive swelling occurs as a result of a transition between a semi-crystalline state to a gel state of the polymer. Under increasing humidity, a critical activity of water is required to induce melting of the crystalline domains in the semi-crystalline PEG. Once this humidity level is reached, an abrupt increase in swelling is expected.

The phase change can be modified if the PEG coatings are enriched with hydrogen molecules. To verify this idea, the PEG sample presented above is exposed to hydrogen gas in a vacuum chamber prior to optical SPR experiments. The hydrogen atoms form bonds with the ether oxygen atoms of the PEG chains [10]. Therefore, fewer ether oxygen atoms are available for the water molecules to make hydrogen bonding during the exposition of water vapour. The decreased interaction of the polymer with the water molecules decreases the response to humidity and the polymer has a more stable structure than before. To attain the phase change, the number of water molecules has to be increased, i.e., the phase change is observed at a higher humidity level. Our measurements on hydrogenated PEG samples show that the hydrogenation of PEG films causes a less pronounced phase change from a semicrystalline state to a gel state.

6. CONCLUSION

The humidity induced changes in the refractive index and thickness of PEG monolayers are determined by optical waveguide spectroscopy. PEG monolayers interact with water strongly and swelling occurs. We can conclude that a single PEG layer is highly hydrophilic and a very large amount of water vapour molecules can be absorbed upon exposure to humid environment, since there is a large increase in the thickness and a large decrease in the refractive index. The changes in the thickness and the refractive index up to 80% relative humidity are gradual due to water intake into the polymer layer. At higher humidity, however, there are abrupt changes in both refractive index and thickness values. This is an indication of a phase change in the polymer from a semicrystalline state to a gel state. Hydrogenation of PEG samples results in a less pronounced phase change from a semicrystalline state to a gel state. Moreover, the phase change is observed to shift to a higher humidity level of 85%.

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