Monitoring of vapor uptake by refractive index and thickness measurements in thin films

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We report a method for real-time monitoring of vapor uptake by simultaneous detection of the refractive index, n , and thickness, d , of thin transparent films with a precision of $\delta n = 10^{-4}$ and $\delta d < 100$ nm. The setup combines total internal reflection (Abbé) refractometry with an interferometric imaging method. A fast Fourier transform and phase fitting method is applied for accurate and independent determination of refractive indices and thicknesses. While the uptake of acetone vapor by polydimethylsiloxane is investigated, the system is also suited for characterization of other solid and liquid films. © 2013 Optical Society of America

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Many industrial materials such as coatings and adhesives readily absorb solvent vapors, which may result in changes of their chemical, mechanical, and optical properties. This uptake of volatile organic compounds (VOCs) either from the gas phase or from an aqueous solution is frequently accompanied by a change in material refractive index (RI) and thickness. While the undesired swelling of thin-film coatings and their RI changes affect their use in harsh environments, the sensitivity of some polymers to solvent vapors can also be exploited for sensing applications [1]. One example is the RI and thickness change in polydimethylsiloxane (PDMS) films when exposed to different VOCs [2,3]. To assess the response of materials to VOCs, it is therefore desirable to design a refractometer that allows for simultaneous measurements of RI and thickness in solid and liquid films while permitting for uptake of either liquids or gases.

Many interferometric measurement methods determine RI and film thickness simultaneously by extracting the optical thickness, $n \times d$, from thin film interference patterns. A Fabry-Pérot (FP) cavity vapor sensor was developed to monitor the reflectance intensity and to calculate the optical thickness change $\Delta(nd)$ of trifluoropropylmethyl silicone when exposed to a variety of organic solvent vapors [4]. FP methods have demonstrated extraordinary sensitivity in independent thickness and RI measurements for films that are applied to a reflective substrate [4,5]. Several similar methods deploy a rotating stage holding a transparent solid plate [6–9]. These systems act as either Mach-Zehnder interferometers or FP cavities that generate fringe patterns under rotation. Algorithms based on peak detection or on Fourier transformation are then used to calculate the RI and thickness, separately. The rotating stage works well for a single-layer solid plate, but liquid samples cannot easily be characterized, and for the purpose of chemical sensing this platform may require redesign of the sample delivery. Reflectometric interference spectroscopy also measures the thin film interference at different wavelengths and obtains the optical thickness, $n \times d$ [10], but cannot measure RI and thickness independently.

Here, we propose a simple and inexpensive method, based on the Abbé refractometer, for simultaneous

and instantaneous RI and transparent thin-film thickness measurements by combining total internal reflection (TIR) and interferometric measurements to monitor the gas uptake in a polymer film. Unlike previous methods, the sample is not placed in the interferometer's optical pathway, nor must it be subjected to rotation relative to the interrogating optical beam. Unobstructed access to the film surface is easily possible, making the method attractive for characterizing liquid and thin films. Solid samples can be exposed to both liquid and gas phases. The precision of the RI and thickness measurements is found to be comparable to that of commercial refractometers (e.g., $\pm 0.0003 n_d$, standard Abbe refractometer, Edmund Optics) and ellipsometers [11,12].

In the setup, a single-mode laser diode (Thorlabs LPS-1550-FC, 1.5 mW) (Fig. 1) is used at 1550 nm. A polarization controller and a polarization filter are used to ensure a vertical linear polarization. Two lenses act as a Galileo beam expander to expand and collimate the light as an ~ 10 mm wide beam. The beam is focused by another lens (focal length: 50 mm) onto the top surface of an uncoated equilateral prism with $n_1 = 1.7434$ at 1550 nm (Edmund Optics, NT47-277). The focal length of the lens, together with n_1 , determines the range of incidence angles. Some of the light is totally internally reflected, and the output is focused by an identical (50 mm) lens such that light originating from different points on the inside surface but at the same reflection angle will be focused on the same line and collected by an IR CCD camera (Edmund Optics NIR camera, NT 56-567) using a PCI-1407 acquisition card (National Instruments). All samples must have an RI

Fig. 1. (Color online) Scheme of refractometer setup and sensing platform.

lower than the prism and are deposited onto microscope slides ($n_{\text{slide}} \sim 1.5$ to 1.74 depending on the sample) and placed on the top prism surface with index-matching fluid ($n = 1.72$).

To observe the changes of RI and thickness when the samples are exposed to solvent vapors, a gas dosing setup was built. Nitrogen is bubbled through the VOC solvent in a wash bottle and then into a two-channel mixing flow meter. The concentration of VOC in N_2 is varied by changing the relative flow rates of saturated vapor and additional dry nitrogen. The gas then flows over the surface of the film from a glass cylinder that is placed on the slide.

TIR on a thick film results in a dark/bright pattern on the detected image [Figs. 2(a) and 2(c)], depending on whether the incidence angle is below or above the critical angle. The intensity of the reflection from a thick film or liquid droplet follows Fresnel's equation accurately (not shown). The camera pixels were calibrated against the angle of TIR at the slide film interface from known RIs of DMSO/ H_2O solutions (dimethyl sulfoxide, Fisher Chemicals, Certified ACS > 95%, concentration 60%–90% v/v, $n_2 = 1.4040$ –1.4507). With $n_1 \sin \theta_i = n_2$ we can calibrate the incidence angle, θ_i , to n_2 , and the pixel row. After calibration, the RI of an unknown sample can be determined by the location of the dark/bright interface, where the accuracy is limited by the resolution of the camera and by image noise. Here, $\theta_i = 52^\circ$ – 56° , and $n_2 = 1.374$ –1.445. With a resolution of about 10^{-4} RI units per pixel and a repeatability of <5 pixels, the accuracy is 5×10^{-4} RI units.

Interference is observed for a thin film of 8.5% polydiphenyl substituted PDMS [Figs. 2(b) and 2(d)], since light is also reflected from the film's top surface. In general, multiple reflections contribute to the interference pattern, but since they lead to the same interferogram, we can simplify the model to that of double-beam interference. The intensity equation is then approximated as

$$I_r = I_o + I_1 \cos(\phi), \quad (1)$$

Fig. 2. (Color online) (a) TIR shows the angular relation of RI, (b) thin film interference allows for determination of the film thickness, (c) the refractometer image of a thick DMSO (75%) liquid layer, (d) an image for a thin polydiphenyl substituted (8.5%) PDMS film, and (e) calculated image from Eqs. (1) and (2) for the film in (d).

with

$$\phi = \frac{2\pi}{\lambda_0} 2n_2 d \cos \theta_t = \frac{4\pi d}{\lambda_0} \sqrt{n_2^2 - n_1^2 \sin^2 \theta_i}. \quad (2)$$

A simultaneous determination of n_2 and d is possible through Fourier analysis. One can determine both values, even if the critical angle falls outside the instrument range and/or the TIR cannot be independently determined. We first extract the phase, ϕ , of Eq. (1) by writing the intensity as

$$I_r = I_0 + \frac{1}{2} I_1 e^{j\phi} + \frac{1}{2} I_1 e^{-j\phi}. \quad (3)$$

The Fourier transform (FT) of I_r is

$$\text{FT}\{I_r\} = I_0 \delta(0) + \frac{1}{2} I_1 \text{FT}\{e^{j\phi}\} + \frac{1}{2} I_1 \text{FT}\{e^{-j\phi}\}. \quad (4)$$

In the FT spectrum, the delta function $\delta(0)$ represents the constant I_0 [Fig. 3(a)]. The spectra at positive frequencies and negative frequencies correspond to $e^{j\phi}$ and $e^{-j\phi}$, respectively.

By performing the inverse FT on only the positive frequencies of Fig. 3(a), $e^{j\phi}$ is recovered and the phase in the interferogram must be “unwrapped” to correct for the π , $-\pi$ boundary conditions [Fig. 3(b)]. The position of the interface due to TIR is apparent as a phase transition point. Rewriting Eq. (2), we obtain a parabolic function for the unwrapped phase. Considering the random offset of the phase unwrapping function, we introduce an offset phase, ϕ_0 , in the following:

$$n_1^2 \sin^2 \theta_i = -\left(\frac{\lambda_0}{4\pi d}\right)^2 \phi^2 + 2\left(\frac{\lambda_0}{4\pi d}\right)^2 \phi \phi_0 - \left(\frac{\lambda_0}{4\pi d}\right)^2 \phi_0^2 + n_2^2. \quad (5)$$

Given the wavelength, λ_0 , it is now straightforward to fit n_2 and d to Eq. (5). Using $n_1^2 \sin^2 \theta_i = a\phi^2 + b\phi + c$, the RI and thickness can be extracted as follows:

$$d = \lambda_0 / 4\pi \sqrt{-a} \quad \text{and} \quad n_2 = \sqrt{c - b^2 / 4a}. \quad (6)$$

We apply the results of Fig. 2(d) in Eq. (1) and obtain Fig. 2(e).

Fig. 3. (Color online) (a) Fast Fourier transform (FFT) of Fig. 2(d) and (b) the unwrapped phase obtained by inverse FFT of the window in (a) and polynomial fit.

Fig. 4. (Color online) Change of film thickness (left) and RI (right) upon exposure to acetone by the polydiphenyl-doped PDMS polymer.

For thick films or rough films, the fringe pattern cannot be analyzed, and we rely on TIR to determine the RI. For example, a film with $n_2 = 1.42$ and $d > 200 \mu\text{m}$ has over 100 fringes in the camera's field of view.

A Visual Basic (Microsoft) program combined with NI Vision (National Instruments) was written to perform the image acquisition, Fourier transformation, windowing, and fitting to Eq. (5) in real time.

PDMS polymers are effective extraction matrices for many volatile organic species and are commonly employed for solid phase microextraction applications [13]. When VOCs are absorbed by PDMS, the RI and thickness change characteristically due to adsorption and film swelling. PDMS can therefore be used as a sensing material on RI sensor platforms such as silicon nanowire ring resonators [14], long period gratings [15], etc. As a proof of concept, we deposit an 8.5% polydiphenyl substituted PDMS copolymer onto a slide and expose it to acetone vapor in a 2.8%–8.4% volume fraction in nitrogen gas (Fig. 4). A detailed description and characterization of the polymer's response is beyond the scope of this Letter, but it is obvious that PDMS reversibly swells by up 4% of its initial volume upon acetone uptake, while the RI decreases from 1.4215 to 1.4203. The lowering of the RI upon acetone uptake is consistent with the trend expected from the Lorenz–Lorentz equation, i.e., when approximating the swollen polymer as a 96:4 mixture of PDMS and liquid acetone [15]. In this approximation one would expect a RI of 1.4188 instead of 1.4203. We also note that we can follow the diffusion and restructuring kinetics of the polymer and identify two different time constants.

While the accuracy of the instrument is limited by its calibration to about 5×10^{-4} RIU, the precision is better than 1×10^{-4} RIU, as was calculated from repeated experiments with N_2 . Similarly, the accuracy of the thickness measurement is within 10% of the thickness, whereas the precision of the thickness measurement was always better than 100 nm; e.g., in Fig. 4 (left) the precision is 22 nm. With the current configuration the film thickness can be measured in the range from about 3 to 150 μm , where the range is limited by the requirement to observe between 1 and ~ 80 fringes. The measurement range for thickness and RI ($n_2 = 1.374$ to 1.445) is limited by the range of incidence angles, i.e., the focal length of the lens, and may be increased at the expense of measurement precision. Details on the characterization of the instrument are given in [16].

In summary, an Abbé refractometer that is equipped with an imaging thin-film interferometer is a convenient and inexpensive device to simultaneously obtain the RI and thickness of thin films. Compared to existing methods, the proposed scheme does not require a wavelength or incidence angle scan, and the setup is capable of characterizing, both liquids and thin films. Furthermore, the solid samples can be exposed to both liquids and gases and their response can be rapidly determined. As for all interferometric measurements, the top surface of the film must be smooth, and this ultimately limits the accuracy of the film thickness measurement. The RI range in Abbé refractometry is limited by the requirement that the RI of the prism has to be higher than that of the sample [9]. It is, however, straightforward to purchase an inexpensive prism with an RI as high as 1.74, which is sufficient for all common polymers, adhesive materials, and solvents.

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