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Optical phase-shift dynamics in surface-modified transparent polymers: Application of wavefront distortion analysis to refractive index (RI)-based sensor development

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ABSTRACT

Optical sensors which are based on slight changes in refractive index (RI) resulting from interaction of an optical substrate with some target species utilize a variety of techniques to quantify the RI modification. Detection schemes based on light propagation within optical fibers measure RI changes by transmission efficiency and/or interferometric techniques. Ellipsometry measures changes in surface RI through amplitude and phase changes for the p- and s- components which alter the angle of reflection for polarized light. An alternate method of relating RI variation to surface adsorption in transparent polymers has been explored using a wavefront sensor of the Shack–Hartmann type. The basic concept has been demonstrated by passing a collimated laser beam through a thin film of polystyrene on glass and analyzing the transmitted wavefront for optical phase-shift of the film relative to the glass in the presence of volatile organic compounds. Changes in magnitude of the overall distortion could be related both to the concentration of the vapor and the solvent/polymer solubility parameter match.

1. Introduction

The majority of spectroscopic techniques utilized in chemical analysis is fundamentally based on absorption of light, where the frequency/wavelength of the absorbance is a function of the differences between quantized energy states. These states are related to some structural feature of the compound, such as covalent bond vibrations (IR spectroscopy), π-bonding conjugation (UV spectroscopy), molecular rotation (microwave spectroscopy), and C&H connectivity effects on local magnetic environment (NMR spectroscopy), among other techniques. Spectroscopy thus depends on the use of intensity-sensitive detectors to quantify variable absorbance. While transparent materials do not absorb visible light, they do induce an optical phase shift in the transmitted light to a degree dependent on sample thickness and refractive index. Optical sensors which are based on detection of the slight changes in refractive index (RI) due to interaction of an optical substrate with some target species utilize a variety of techniques to quantify the RI modification. Early detection schemes were based primarily on light propagation within single-mode optical fibres, where RI changes on the fibre surface can be measured by evanescent-wave induced loss of transmission efficiency, or on planar Mach–Zehnder interferometers where differential phase-shifts between beam paths can also attenuate the transmission intensity [1]. The development of microstructured optical fibres (MOFs), also known as photonic crystal fibres (PCFs) or photonic bandgap fibres (PBFs) has allowed increased evanescent-wave interaction by penetration of the target species through the air channels in the core/cladding region [2]. Coupling such PCFs with standard single-mode fibres in a Mach–Zehnder configuration gave a gas sensor with refractive index resolution of approximately 4×10^{-7} [3]. Long-period-gratings (LPG) in both single-mode solid fibers and photonic bandgap crystal fibers have also been investigated for measurement of very small changes in refractive index [4]. LPG-based refractive index optical biosensors [5,6] and gas sensors [7] have been described.

As a stand-off, reflective technique with relatively simple optics, ellipsometry has also been extensively studied for biosensor applications [8–10]. Ellipsometry measures changes in polarization as light reflects from a material surface, with the measured response dependent on optical properties such as RI, and sample thickness. When linearly-polarized light is used, the reflected light undergoes amplitude and phase changes for both the p- and s- components and these changes alter the polarization angle. For biosensor applications the reflective surface is coated with a biological material with specific binding behavior toward some particular molecule and changes in the angle of reflected polarization correlated with target species concentration.

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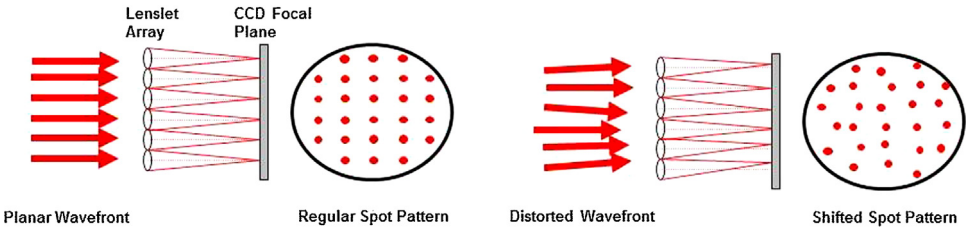

Fig. 1. Operation of a Shack–Hartmann device showing spot pattern changes for planar vs. distorted wavefronts.

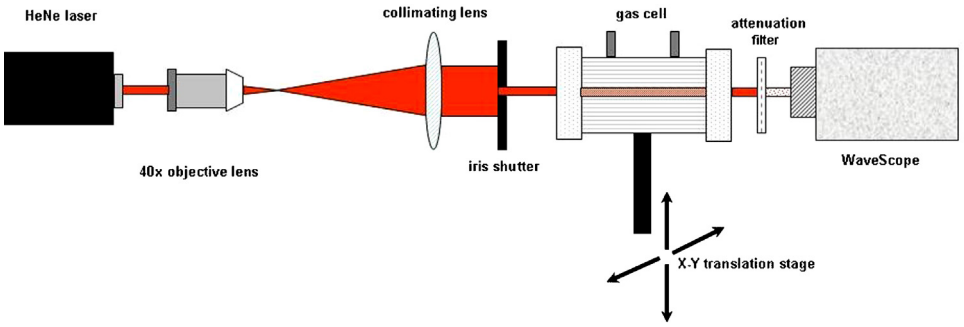

Fig. 2. Configuration of wavefront distortion analysis equipment.

An alternate method of utilizing slight variations in refractive index for quantifying changes in optical behavior lies in transmission of light through transparent materials. When the transparent solid has a non-uniform refractive index, differential phase retardation related to sample inhomogeneity results in a distorted wave front for the transmitted beam. This phase distortion may be mapped by a single-beam interferometer of the Shack–Hartmann type [11–13], which operates by dividing the aberrated wave front into multiple sub-apertures by a grid of microlens ("lenslets"). The spot pattern from the microlens on a CCD focal plane can be analyzed to quantify both the degree and direction of the localized wavefront tilt (see Fig. 1). While phase-sensitive detectors are the fundamental basis for optical wavefront analysis in such diverse fields as laser eye surgery [14] and telescope image enhancement [15], application of the general concept to chemical analysis has been almost completely unexplored. Survey of the literature shows only a few examples of Shack–Hartmann wavefront analysis for optical study of material properties, and these relate primarily to examining laser-induced thermal distortion effects [16–18]. Research at the EMU Laser Physics Laboratory has successfully utilized a S-H wavefront analyzer in development of a novel optical method for monitoring the degree of fusion of PVC plastisols [19]. Continuing work aimed at design of novel optical sensors has now shown that changes in refractive index related to absorption of organic vapors by a transparent polymer film result in changes in the transmitted wavefront distortion pattern that can be correlated to both vapor concentration and solubility parameters.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Chemical Company. Ethyl acetate, hexane, anhydrous ethanol, and all other solvents were reagent grade and used without further purification. The polystyrene (PS) was a 280,000 M_W with T_g = 100 °C.

2.2. Equipment

The Shack–Hartmann instrument used in this study was a WFS-01 WaveScope wavefront sensor from Adaptive Optics Associates, Cambridge, MA with a main aperture of 20 mm. The 0300S lenslet module with a 100 × 100 grid of square lenses of 300 micron pitch (~10–11 lens per mm^2) and an EFL (effective focal length) = 15.8 mm was used for wavefront imaging. With a 6 mm diameter beam spot, the 0300S module yielded ~315 data points per image. A randomly polarized JDS Uniphase Model 1508 0.5 mW, 633 nm HeNe laser was the beam source. Lens, attenuators, mounts,

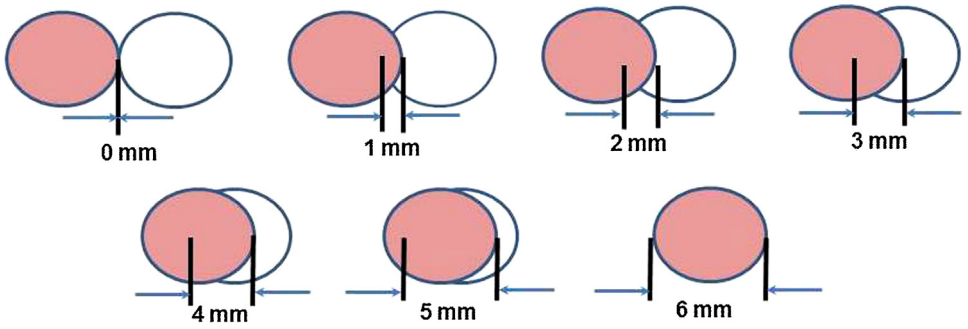

Fig. 3. Beam-film spot overlap settings for baseline RMS values.