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Gas sensing using polymer-functionalized deformable Fabry–Perot interferometers

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ABSTRACT

We report a chemical vapor sensor in which polymer swelling, upon analyte absorption, is used to deform an on-chip silicon Fabry–Perot interferometer (FPI). The magnitude of the deformation, recorded through the resonance wavelength shift, is proportional to the analyte concentration in accordance with a simplified analytical model and with finite element simulations. Conventional and phenyl-doped polydimethylsiloxane (PDMS) polymers are used to functionalize different interferometers, which are tested for the detection of two volatile organic compounds, i.e. m-xylene and cyclohexane. The detection of m-xylene concentrations down to 34 ppm—limited by our flow-meter setup—is achieved experimentally. Based on the sensitivities and the noise characteristics of the devices, limits of detection (LODs) of 1.6 ppm m-xylene and 6.3 ppm cyclohexane are expected.

1. Introduction

Upon analyte absorption, many polymers (e.g., PDMS) are known to expand [1], a phenomenon usually referred to as “polymer swelling”. Such expansion can be used to deform optical interferometers, causing a shift of their resonance condition that can be monitored to create chemical sensors. This approach was previously used with various optical interferometers. Polymer-coated fiber Bragg gratings were shown to deform upon exposition to salt [2] hydrocarbons [3] and humidity [4]. Bragg gratings were also fabricated directly with deformable polymer layers and were found to be sensitive to the presence of acetone [5], salt [6], and volatile organic compounds [7] (VOCs). Fabry–Perot interferometers (FPI) can also be formed simply by exploiting reflections at the two material interfaces of single deformable polymer membranes. This approach was used to detect VOCs [8–10] and ionic strength [11].

The sensors reported here rely on deformable Fabry–Perot interferometers. As presented in Fig. 1, these FPIs are implemented in-plane with the substrate by vertical plasma etching of silicon-air Bragg reflectors. The in-plane (i.e.: vertical mirrors, in-plane optical axis) rather than out-of-plane [5–11] configuration allows monolithic integration of microfluidic systems and optical fiber alignment grooves. Integrated microfluidic systems simplify the parallel functionalization of multiple interferometers, using different polymers, to target specific classes of analytes. Fiber grooves allow the remote interrogation of the interferometers with passively aligned conventional single-mode optical fibers, rather than requiring free space alignment of light sources and photodetectors [5–11].

2. Methodology

2.1. Sensing mechanism

Upon analyte absorption, three factors can cause shifts of the interferometer ($\Delta\lambda_{\mathrm{Res}}$) resonance wavelength. First, as depicted in Fig. 1(b), polymer swelling deforms the interferometer, resulting in an increase (ΔL) of the mirror separation (L). This mechanism will later be demonstrated to be the dominant one. Secondly, if the refractive index of the analyte (n_a) and the polymer (n_p) are different, the refractive index of the polymer–analyte mixture (n) should change by a factor Δn_{Mix} upon sample absorption. Lastly, if the mirrors oppose a significant force to the polymer expansion, there should be a densification of the polymer, which should lead to a Δn_σ variation of its refractive index. All three effects change

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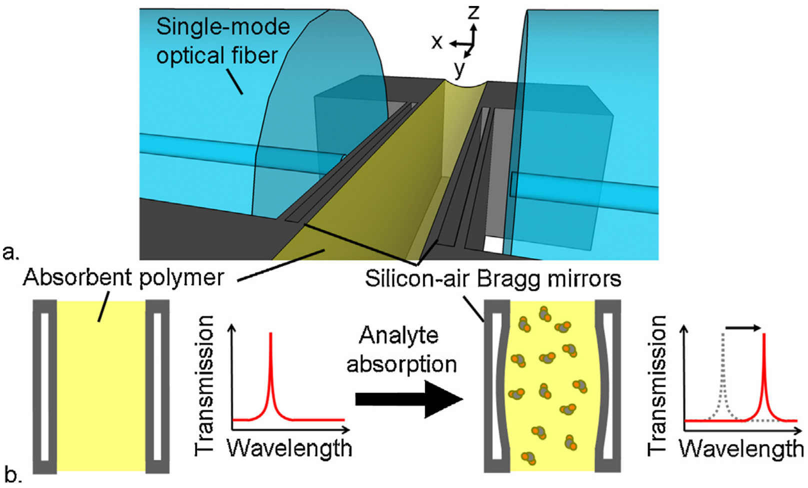

Fig. 1. (a) Schematic representation of the deformable interferometric sensor. (b) Schematic representation of the sensor operation principle. Upon sample absorption, polymer expansion deforms the interferometer, inducing a shift of its resonance wavelength. Refractive index changes in the polymer, upon absorption, also contribute to this shift.

the interferometer optical pathlength (nL), and contribute to the measured resonance wavelength shift ($\Delta\lambda_{\text{Res}}$) through:

$$\frac{\Delta\lambda_{\text{Res}}}{\lambda_{\text{Res}}} = \alpha\frac{\Delta L}{L} + \beta\frac{(\Delta n_{\text{Mix}} + \Delta n_{\sigma})}{n}, \qquad (1)$$

where $\alpha = 0.75$ and $\beta = 0.93$ are device-specific reduction factors (≤ 1). The factor α accounts for the fact that only one layer in each Bragg mirror is displaced upon analyte absorption (see Fig. 1b). The factor β accounts for the fact that the resonant mode inside the cavity is not located entirely inside the polymer, but also partly inside the mirrors (i.e., the thickness of the mirrors is not negligible compared to L, the distance between the mirrors). The value of both parameters can be calculated using a previously reported optical simulation algorithm for deep-etched Fabry–Perot interferometers [12], as detailed in Appendix A1.

We define the dimensionless sensitivity (Γ_{ϕ}) as the normalized ratio of the resonance wavelength shift ($\Delta\lambda_{\text{Res}}$) to the absorbed volume fraction of analyte (ϕ_a) inside the polymer:

$$\Gamma_{\phi} = \frac{1}{\lambda_{\text{Res}}}\frac{\Delta\lambda_{\text{Res}}}{\Delta\phi_a} \qquad (2)$$

Conveniently, ϕ_a can be related to the volume/volume (v/v) concentration of analyte in air (C_{air}), near the polymer, using the ideal gas law and the partition coefficient of the polymer for the respective analyte (K_{p-a}):

$$\phi_a = K_{p-a}\frac{PV_{\text{m}}}{RT}C_{\text{air}} \qquad (3)$$

where P is the pressure (1 atm in our case), T is the temperature, R is the gas constant, and V_{m} is the molar volume of the analyte, in liquid phase.

For all the calculations presented in this work we assume that upon absorption, the final volume of the polymer–analyte mixture equals the initial volume of the polymer, plus the absorbed volume of analyte. In other words we assume that there is no volume reduction upon absorption, except in the presence of mechanical stresses inside the polymer (calculations in Section 2.1.1 will demonstrate these stresses lead to negligible volume reductions). In this context, the relative volume (V) expansion of the polymer upon absorption of a ϕ_a volume fraction of analyte is given by:

$$\frac{\Delta V}{V} = \Delta\phi_a \qquad (4)$$

This assumption of volume additivity is supported by reports that the absorption of a slightly lower refractive index analyte (cyclohexane) reduced the refractive index of a PDMS-based polymer [13]. This would not have been possible if significant volume reduction occurred upon absorption, since volume reduction would have led to an increase of the refractive index.

2.1.1. Simplified analytical model

This section details the sensitivity (Γ_{ϕ}) of deformable FPI sensors in the case where:

(1) the mirrors are perfectly movable, such that they oppose negligible forces to the expansion of the polymer,
(2) the volume increase of the polymer (i.e. swelling) is directed mainly in one direction, parallel to the optical pathlength between the mirrors (L), such that ΔL is maximized.

Interestingly, these conditions straightforwardly apply to out-of-plane deformable Fabry–Perot interferometers [8–11]. In these cases, the polymer is bonded to a rigid substrate such that swelling can only occur in the out-of-plane direction, which is parallel to the optical axis (criterion 2). There is also no force opposing the movement of the top material interface that is used as the movable mirror of the interferometer (criterion 1).

For the in-plane devices presented in the current work (Fig. 1), compliance with the two above mentioned criteria is less trivial. The deformable layer in each Bragg mirror might oppose non-negligible force to the expansion of the polymer. The polymer might also swell upward (positive z direction in Fig 1a) if the bonding strength with silicon is not strong enough. We will therefore use the simplified ideal formalism presented in this section primarily as a basis for comparison of our in-plane sensor with out-of-plane sensing mechanisms. In Section 2.1.2 finite element simulations will address the limitations of the analytical model for in-plane devices.

Under the two conditions listed above, it is possible to show that the relative length increase between the mirrors, upon absorption of a ϕ_a volume fraction of analyte, is given by:

$$\left.\frac{\Delta L}{L}\right|_{\text{Simplified}} = \frac{\Delta\phi_a}{3}\frac{1+\nu}{1-\nu} \qquad (5)$$

where ν is the polymer Poisson's ratio. It is also possible to show that the compressive stress experienced by the polymer due to its