

Polymer Bragg Filters for Organic Solvent Detection

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We present Bragg filters fabricated from cross-linked optical standard polymers. The filters have been characterized by measuring their transmittance in the visible and near-IR spectrum. Upon the presence of organic solvents in the surrounding atmosphere, the polymer layers swell and cause the filter peak shift to a higher wavelength.

1 Introduction

Bragg filters consist of a central optical layer (the cavity) enclosed between two multilayer Bragg mirrors (see Fig. 1). The transmittance spectrum of such a device is given by the combination of the Fabry-Perot cavity resonances combined with the highly wavelength-dependent reflectance of a Bragg mirror. Together, these effects result in a sharp filter peak. By an appropriate choice of the refractive index and thickness of the layers involved, the transmittance maximum of a Bragg filter may even be designed to a desired wavelength. Tuning of a Bragg filter may be accomplished by changing the angle of incidence of the transmitted light, or by changing the refractive index and l or the thickness of the optical layers by appropriate physical effects.

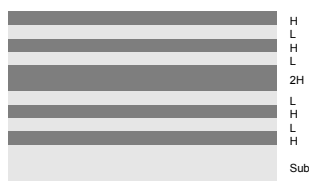


Fig. 1 General structure of a Bragg filter. H (resp. L) means a $\lambda/4$ -layer of the high index (resp. low index) material.

Tunable Bragg filters play an important role in a number of applications such as optical telecommunications and astronomy. Different approaches for their fabrication have been proposed and fabricated. These rely mainly on semiconductor process technology and comprise silicon technology [1] as well as III-V-technology [2].

In this paper, we present a novel approach for fabrication of Bragg filters from polymers. Furthermore, we demonstrate that the transmittance maximum of the filters may be shifted by polymer swelling in solvent-containing atmosphere.

2 Fabrication

For the fabrication of the filters we used optical standard polymers, polymethylmethacrylate

(PMMA; $n_D = 1.49$) and polystyrene (PS; $n_D = 1.59$). These polymers have been chemically modified to allow photo-cross-linking of the polymer chains. Filters were fabricated by repeated spin-coating and UV-photo-cross-linking a multiple layer stack on a glass substrate. The filter structure was substrate-(HL)⁸-2H-(LH)⁸-H, where H stands for a $\lambda/4$ -layer of PS and L for a $\lambda/4$ -layer of PMMA. We choose a wavelength of 600 nm for the transmittance maximum.

The ability of cross-linking the polymers is a decisive feature for the spin-coating based fabrication process, because cross-linking prevents the layers from dissolution and delamination.

3 Fundamental characterization

The fabricated Bragg filters have been characterized by measuring their transmittance in the wavelength range from 400-1400 nm. All spectra shown in this paper are spectra of the complete device including the substrate.

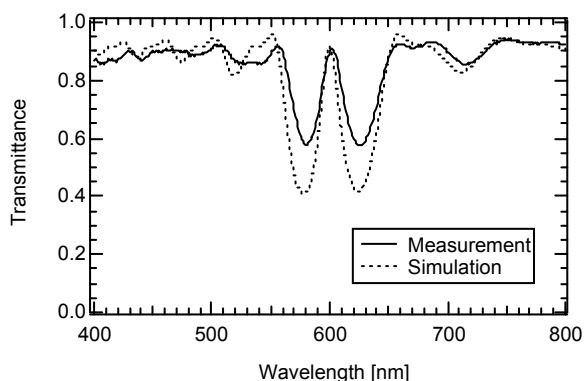


Fig. 2 Measured and simulated transmittance spectra of a polymer Bragg filter.

We compared the experimental results to simulated spectra. The simulations are based on Fresnel matrix formalism as described in standard optics textbooks [3]. The comparison shows that the filter peak is less pronounced in the experiments than expected from theory, see Fig. 2. We attribute this discrepancy to the mutual inter-diffusion of the

polymer chains, resulting in a finite width of the interface with a gradual change in refractive index.

4 Filters in the presence of solvents

Organic solvents in the atmosphere surrounding the filters cause the cross-linked polymer networks to swell. Swelling of cross-linked polymer networks may be understood by a balance of elastic energy due to deformation of the polymer network and mixing entropy due to mutual diffusion of the polymer chains and the solvent molecules into each other. For surface-attached polymer networks, as is the case with our filters, the thickness of the layer increases, i.e. swelling is perpendicular to the surface. By swelling, the thickness of a polymer layer may increase by several 100%.

On the other side, also the refractive index of the polymer layer is affected by swelling: It changes towards the refractive index of the solvent. This is described by Lorentz-Lorenz-theory.

In summary, both effects lead to a dramatic “red-shift” of the filter peak wavelength. Fig. 3 shows transmittance spectra of a filter at several partial pressure values (given as a fraction of the saturation value) of acetone in nitrogen.

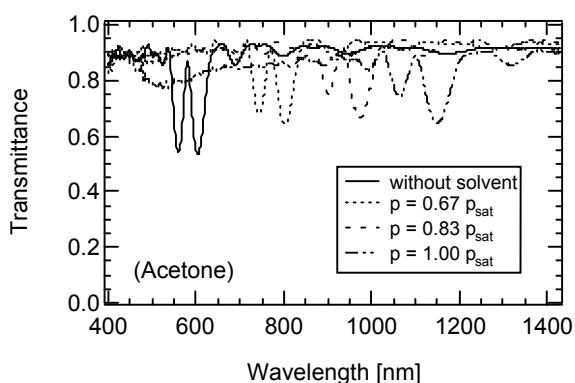


Fig. 3 Filter transmittance spectra at several partial pressure values of solvent in the atmosphere.

5 Polymer Bragg filters as solvent sensors

In the experiments we found that the saturation value of the transmittance peak wavelength corresponds to a solvent-saturated atmosphere. From this observation and by making use of the linear dependence of the transmittance peak shift on the solvent concentration in the atmosphere, we may calculate a filter sensitivity in units of picometers (wavelength shift) per ppm (solvent concentration). The estimated filter sensitivities to several solvents can be found in Tab. 1.

Solvent	Acetone	Ethanol	Toluene	THF
Sensitivity [pm/ppm]	2.5	2.8	16.4	3.9

Tab. 1 Estimated filter sensitivity from the experiments.

For the use of polymer Bragg filters as solvent sensors, the response time to changes in the solvent content of the atmosphere is a further important question. In Fig. 4, we show the filter response upon taking the filter out from a vessel with saturated (toluene in nitrogen) atmosphere into the solvent-free ambient atmosphere. By considering the time required for taking a transmittance spectrum, we conclude that the response time of the filter is at maximum the exponential time constant found in this experiment, which is (8.8 ± 0.4) s. This is a value which allows using polymer Bragg filters as optical solvent sensors.

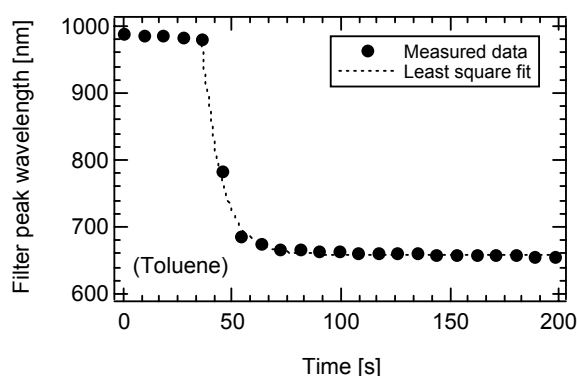


Fig. 4 Filter response upon an instantaneous change from saturated to solvent-free atmosphere. The exponential time constant in this experiment is (8.8 ± 0.4) s (from least square fit to data).

6 Conclusion and outlook

From the data described here, we conclude that polymer Bragg filters are an interesting tool for spectroscopic measurement of concentrations of chemical species.

In the experiments presented here, swelling of the optical layers is unspecific to the solvent species. However, chemical modifications of the polymer chains could open a way to specific interactions and quantitative analysis of certain species.

References

- [1] D. Hohfeld and H. Zappe, “An all-dielectric tunable optical filter based on the thermo-optic effect,” *Journal of Optics A: Pure and Applied Optics* **6**, 504–511 (2004)
- [2] J. Daleiden, V. Rangelow, S. Irmer, F. Römer, M. Strassner, C. Prott, A. Tarraf, and H. Hillmer, “Record tuning range of InP-based multiple air-gap MOEMS filter,” *Electronics Letters* **38**, 1270–1271 (2002)
- [3] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, Oxford, 6th corrected ed. 1993).