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Planar Bragg Grating Sensors Functionalized with Cyclodextrins for Trichlorofluoromethane Sensing

Stefan Belle[1], Stefan Kefer[1], Siegfried R. Waldvogel[2] and Ralf Hellmann[1]
[1]Applied Laser and Photonics Group, Aschaffenburg University of Applied Sciences, Wuerzburger Strasse 45, 63743 Aschaffenburg, Germany
[2]Instiitute of Organic Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55125 Mainz, Germany
Corresponding author's e-mail address: ralf.hellmann@th-ab.de

Summary:
This contribution summarizes on recent findings of planar Bragg grating sensors, functionalized with cyclodextrins, for the detection of ozone depleting trichlorofluoromethane. Detection limits as low as 5 ppm are feasible whereas sensitivity and dynamic depend on the employed cyclodextrin class. The prospect of transferring the technology from silicas to polymer-based devices is also presented.

Keywords: Optical Sensor, Bragg Grating, Evanescent Field, Cyclodextrin, Trichlorofluoromethane

Introduction

Once an auspicious chlorofluorocarbon, widely employed as propellant and refrigerant, the usage and fabrication of trichlorofluoromethane, also referred to as CFC-11 or R-11, is now strictly prohibited due to its vast ozone depletion potential [1]. Nevertheless, the substance is still released nowadays, for example during the recycling of obsolete cooling devices or even in illegal production plants [2].

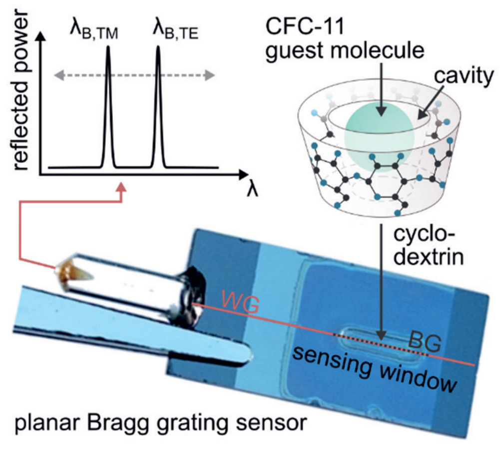

Fig. 1. Working principle of a planar Bragg grating sensor functionalized for CFC-11 sensing via cyclodextrin coatings.

Thus, reliable and sensitive detection of CFC-11 is still of vital importance for the society and yet continuously a technological challenge for modern sensors. Optical Bragg gratings constitute a promising technology for this task, since, besides low weight, they offer outstanding electromagnetic, chemical and thermal resistance. However, they necessitate functionalization for the detection of CFC-11, which can be achieved by coating the sensitive Bragg grating region with cyclodextrins (CDs). Due to their molecular structure and composition, CDs are able to form a non-covalent host-guest complex with CFC-11, as illustrated in Fig. 1. Coating a planar Bragg grating (PBG) device with CDs enables quantification of the CFC-11 molecule abundance via the evanescent field interaction of guided mode and functional coating, which leads to a shift of the PBG's modal Bragg reflection peaks $\lambda_{B,TE}$ and $\lambda_{B,TM}$. Based on their composition, CDs are classified as α-, β- or γ-cyclodextrin. Further modification of its solubility, viscosity and selectivity, is adapted by substitution of the CD's hydroxyl groups.

Sensor Response

An overview of the employed CD derivatives is given in Tab. 1 , while Fig. 2 depicts the respective Bragg wavelength shift $\Delta\lambda_B$ of both modal reflection peaks as a function of the CFC-11 content, diluted in nitrogen. It is found that, in all cases, the maximum response of the TE reflection peak is about ten times larger than that of the TM signal. *Per*-methyl substituted derivatives exhibit maximum wavelength shifts up to

Tab. 1: Per-substituted cyclodextrin derivatives.

Substitute	α-CD	β-CD	γ-CD
Methyl	CD1	CD2	CD3
Ethyl	CD4	CD5	CD6
Allyl	CD7	CD8	CD9

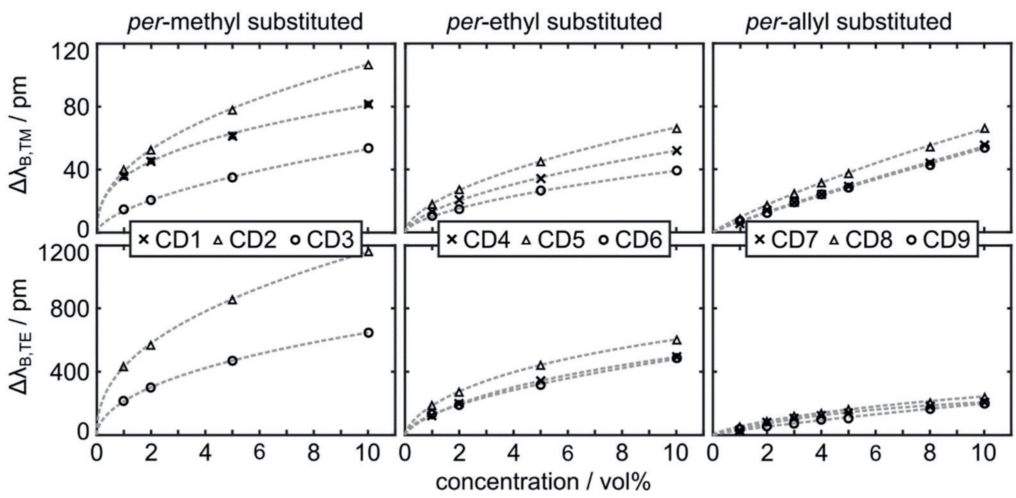

Fig. 2. Bragg wavelength shift of both modal (TE & TM) reflection peaks as a function of CFC-11 concentration in nitrogen, for α-, β- or γ-cyclodextrin derivative coatings with various hydroxy substitutions.

1200 pm (CD2), which results in a detection limit of 5 ppm. This value is about 400 times larger than that of an uncoated PBG. The signal deflection of *per*-ethyl- and *per*-allyl substituted derivatives, however, is reduced. Albeit, in contrast to the determined sensitivities, these derivatives show a significantly faster temporal response when the sensor is exposed to CFC-11 in nitrogen. For example, the rise times for CD2, CD5 and CD8, at 1 vol% CFC-11, are 1435 s, 71 s and 45 s, respectively. Consequently, it is feasible to tailor the functionalized PBG's behavior by employing the appropriate CD coating [3].

Spontaneous Crystallization

Exposing a PBG coated with CD1 to a CFC-11 content of at least 35 vol% leads to spontaneous crystallization of CFC-11 on the surface of the PPBG, as depicted in Fig. 3.

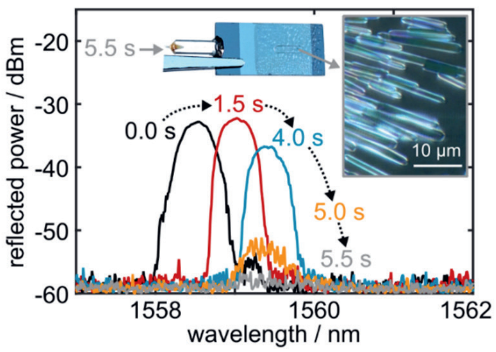

Fig. 3. Signal loss due to spontaneous crystallization. Inset: Sensor with crystallized surface and microscopic image thereof.

Within a timeframe of 5.5 s, this leads to complete signal loss due to a drastic refractive index increase of the functionalization coating and / or scattering losses by the structural reconfiguration of the crystallized surface [4].

Conclusion and Outlook

In conclusion, PBGs functionalized with CDs are well-suited for the detection of volatile trichlorofluoromethane, whereas sensor sensitivity and response time can be adapted by employing appropriate CD derivatives. CFC-11 quantities above 35 vol% lead to spontaneous crystallization of the coating which can be exploited for the development of new filter and storage concepts [5]. While all PBGs used in this study are SiO_2 based, future research will focus on transferring the demonstrated methodology on polymer-based planar devices and the development of new affinity materials.

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