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An integrated optical Bragg grating refractometer for volatile organic compound detection

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ABSTRACT

We report an integrated optical Bragg grating detector, fabricated using a direct UV-writing approach, that when coated with a thin-film of a hydrophobic siloxane co-polymer can perform as an all-optically accessed detector for hydrocarbon vapour. Upon exposure to a series of organic solvent vapours, both negative and positive Bragg wavelength shifts of differing magnitudes were measured. This was attributed to a combination of swelling and/or hydrocarbon solvent filling the free volume within the polymer film. A quantitative structural property relationship (QSPR) approach was utilised to create a multiple variable linear regression model, built from parameters that chemically described the hydrocarbons and the intermolecular interactions present between the co-polymer and hydrocarbon molecules. The resulting linear regression model indicated that the degree of swelling of the polysiloxane thin film when exposed to vapours of different hydrocarbons was due to the physico-chemical properties of the hydrocarbons and that this was the main causative factor of the measured Bragg wavelength shifts. Furthermore, this linear regression model allows for the prediction of the Bragg wavelength shift that would be measured upon exposure to vapours of another defined hydrocarbon. This detector is intrinsically safe in flammable environments. It includes on-chip thermal compensation, operates at telecoms wavelengths and has a predictable response to a variety of hydrocarbons making it ideal for detection of flammable hydrocarbon vapours in industrial and domestic processes.

1. Introduction

The detection of volatile organic compounds (VOCs), including hydrocarbons, is required to ensure legislative and safety targets are met in industrial environments. Hydrocarbon emission can occur on the large scale during industrial processes, and on the smaller scale in systems ranging from vehicles powered by combustion engines [1] to the use of adhesives and paints [2,3]. In situations such as industrial manufacturing plants that frequently contain explosive atmospheres it is a legal requirement that any measuring techniques be intrinsically spark-free [4].

One of the earliest devices for gaseous hydrocarbon detection was the 'Davy lamp', which revolutionised mining by allowing safe operation within potentially explosive environments [5]. More contemporarily, the most common portable detectors are Photo-Ionisation Devices (PIDs) [6]. Such detectors can achieve sub-ppm accuracy, but cannot provide continuous monitoring and the operator is exposed to potentially hazardous environments to take measurements [6]. Remote sensing can be achieved with other detection techniques, such as infrared open-path detection [7], however, this method can be cross-sensitive to dust clouds or vapour mists, which cause optical scattering losses and may lead to false positives. In contrast, optical fibre sensors do not suffer from optical power losses caused by dust and vapour mists, are intrinsically suitable for use in hazardous or explosive environments, and can be operated at standard telecoms wavelengths. Indeed, there are many examples in the literature of optical fibre gaseous hydrocarbon detectors and sensors, such as optical absorption-based sensors [8–11]. In contrast, relatively few examples of integrated optical sensors—planar lightwave circuits that contain several optical components which are combined to fulfil

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the sensing/detection function—have been reported for detection of hydrocarbons, despite the advantages of these over optical fibre-based sensors which include on-chip thermal compensation, the potential to combine multiple optical functions in a single device for multi-parameter analysis, [12,13] and the ability to remotely interrogate large multi-sensor arrays *via* optical fibre interconnects [14].

In the literature, hydrocarbon sensors have been modified with polymer thin-films that swell in the presence of hydrocarbon vapour, where the coupling of this swelling to electrochemical, mechanical or optical transduction technologies affords the output signal [15–21]. Thundat *et al.* reported a microring resonator integrated optical sensor, coated with a layer of poly(dimethylsiloxane) (PDMS). The PDMS swelled in the presence of ethanol and acetone vapours, causing the thickness and permittivity of the layer to change which resulted in a shift of the measured resonant frequency [21]. Similarly, Lowe *et al.* utilised the swelling of polymer layers to develop a planar holographic sensor for a wide range of hydrocarbon vapours. The authors demonstrated that the holographic response, upon exposure to range of volatile organic compounds, could be explained by the Hildebrand solubility parameter in a non-linear manner [22]. Here, we investigate the efficacy of a polysiloxane layer as the active element in an integrated optical VOC detector with a diverse range of hydrocarbon solvents. The relationship between the refractive index of the swollen polymer layer with the properties of the solvents is probed by a quantitative structural property relationship (QSPR) linear regression model, enabling prediction of the sensor response to a test set of hydrocarbons.

2. Background

A Bragg grating is a periodic modulation of refractive index along a waveguiding channel, which in reflection acts as a wavelength-selective reflector. Bragg gratings are inherently sensitive to both temperature and strain, however if the light within the waveguide is able to interact with the local environment, then evanescent coupling allows for a measurable change in the optical characteristics [23]. Changes in this environment alter the effective refractive index, n_{eff} of the Bragg grating and result in a corresponding shift in the Bragg wavelength (λ_B). Here, an integrated optical refractometer (Fig. S1a) was fabricated by simultaneously 'writing' both the waveguide and Bragg gratings with a UV-laser directly into a planar photosensitised silica-on-silicon substrate, without the need for photolithographic processing [24–27]. Each Bragg grating functioned as an independent refractometer, capable of detecting changes in the refractive index near the surface *via* the corresponding spectral shift in the Bragg wavelength with sub-picometre precision (Fig. S1b). A thorough review of the fabrication of these planar integrated Bragg gratings devices using the direct UV-writing approach is given by Holmes *et al.* [28].

It has been shown previously that these devices are sensitive to physisorbed water on the surface of the exposed waveguides [29] and, upon functionalisation with a mesoporous aluminosilicate thin-film, they are capable of monitoring relative humidity in real-time [30]. Here we exploit the differing permeability of an amorphous polymer film to hydrocarbon vapours to gain both sensitivity and specificity. Hydrocarbon vapours will solvate the polymer layer and the degree of solvation is specific to each analyte. This will determine the extent of swelling of the polymeric layer and consequently the measured refractive index of the polymer will change. It is noted that Hellmann *et al.* have reported a silica-on-silicon optical Bragg grating sensor for the detection of vapours of naphthalene, benzene, toluene and *m*-xylene, *via* a multi-layer film of γ-cyclodextrin [31,32]. However, the generalisability of their sensor is hindered by the limited host-guest selectivity of the γ-cyclodextrin macrocycle and the effect of binding constants was not discussed [33].

3. Results and discussion

3.1. Integrated optical Bragg grating refractometer

An integrated optical Bragg grating device (BGD) comprising of a channel waveguide containing eight spectrally distinct Bragg gratings was fabricated (Fig. 1a). The corresponding reflectance spectrum of the uncoated device is shown in Fig. 1b, with a distinct spectral peak for each of the eight Bragg gratings. The central four Bragg gratings were designated for sensing, while the peripheral Bragg gratings (1540 nm and 1565 nm, marked with an asterisk in Fig. 1b) were used for self-referencing against environmental fluctuations, principally temperature. The Bragg gratings at the extremities of the device (1535 and 1570 nm), while still suitable for temperature referencing, exhibited spectral fringes, due to interference effects, which degrade the quality of peak fitting. As such, these gratings were not used explicitly for referencing in the following work, but did allow for further confirmation of observed thermal trends.

The sensor region of the BGD was spin-coated with a thin-film of poly(hydroxymethyl-*co*-octylmethyl)siloxane (POHMS). As detailed in the Supplementary Information, POHMS was successfully synthesised *via* a hydrosilylation reaction with poly(hydroxymethyl)siloxane (PHMS). The resulting co-polymer contained 15 mol% of the octylmethyl monomer, as confirmed by NMR and FTIR spectroscopy. The differing hydrophobicity (corresponding to swelling ability [34]) of the two monomer components was anticipated to enable sensitivity to a wider range of solvent vapour than for a homogenous polymer. The refractive index of the co-polymer was measured as 1.4397 ± 0.0005 at 1553 nm wavelength (Metricon 2010/M prism coupling refractometer), with the film thickness approximately 1.4 μm as measured by scanning white light interferometry [35]. As the thickness of this polysiloxane film is expected to be far greater than the extent of the evanescent field of the guided optical mode perpendicular to the surface of the device [36], any measured change in refractive index (after thermal compensation) should be exclusively due to solvent-triggered changes in the POHMS layer.

3.2. Solvent vapour sensing

The BGD was mounted within a gas flow cell and optically interrogated whilst exposed to either a flow of dry nitrogen carrier gas or a flow of nitrogen carrier gas saturated with solvent vapour, with the temperature independently monitored *via* a thermocouple. The carrier gas was enriched at a temperature 20 K higher than the boiling point of each solvent, with the flow cell being held at 301 K throughout. This gas sensing apparatus was based on previously reported organic vapour sensing experiments [37,32], and the protocol is described in detail in the Supplementary Information and schematically in Fig. S2. The device was exposed to saturated vapour from a diverse set of fifteen solvents: methanol (MeOH, 19.3%), acetone (Acet., 34.2%), *n*-hexane (n-hex, 22.8%), isopropyl alcohol (IPA, 6.9%), dichloromethane (DCM, 63.7%), cyclohexane (CY, 14.6%), cyclohexene (CH, 13.3%), benzene (Benz.,14.3%), carbon disulfide (CS_2, 52.6%), ethyl acetate (EA, 14.2%), chloroform ($CHCl_3$, 29.4%), tetrahydrofuran (THF, 24.2%), toluene (Tol., 4.3%), oct-1-ene (O-1-E, 2.7%), 1,4-difluorobenzene (1,4-dfb, 9.7%) and water (H_2O, 3.7%). The reported proportion of each solvent dispersed in 100% saturated nitrogen at 301 K is given in parenthesis above [38].