Foil-based optical technology platform for optochemical sensors

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ABSTRACT

This paper describes the development of a low-cost technology platform for fluorescence-based optochemical sensors. These sensors were constructed by incorporating fluorescent sensing elements in the core of multimode waveguides or lightguides, and have applications in medical, biochemical and environmental diagnostics. Flexible lightguides were fabricated either with silsesquioxane-based or PDMS-type optical polymers using photolithography or soft-lithography based replication techniques respectively. Spectral transmission characteristics were measured along with loss values obtained by cut-back measurements for several wavelengths from visible to mid-IR. Propagation losses as low as 0.14dB/cm were measured for 50 x 50 μm^2 waveguides. For coupling light in and out of the waveguides, different types of coupling structures, e.g. 45º micromirror plugs were investigated.

Keywords: fluorescence, foil, optochemical sensor, polymer waveguides

1. INTRODUCTION

Optochemical sensors involving a diverse scheme of sensing strategies have been employed in detecting presence and concentration of a wide range of analytes and have applications as diverse as medical and biochemical fields to security systems and food-packaging industry[1]. A very wide range of technologies are available in sensing analytes each having its own advantages and disadvantages. The early forms of the flame-safety lamps[2] to the modern catalytic detectors[3] are all manifestations of a combustible gas sensor. Late 1980s saw a large boom in sensors made of semiconducting materials, which were promising for obtaining low-cost gas detector[4]. The whole class of metal oxide sensors to surface acoustic wave sensors[5] provided strategies to tackle the sensing problem, but it was clear that the solution would be problem-specific.

Fluorescence is an important transduction mechanism for the detection of chemicals[6]. Fluorescence microscopy and spectroscopy techniques using life-time, anisotropy, or fluorescence intensity offers much promise in this area[7]. Fluorescence sensing has many advantages such as high sensitivity, capability of continuous and remote monitoring, use of minimal amount of analytes and often reversibility. Despite having fluorescent sensors based on polymers[8], sol-gel materials[9], mesoporous materials[10], surfactant aggregates[11], nanoparticles[12] and many combinatorial methods, a continuous and reversible sensor intended at many different targets still remains a quandary open to tackle.

A new sensor concept is proposed that applies a low-cost and foil-based optical technology platform for multi-analyte detection. Such a sensor makes use of changes in fluorescence behavior of dyes in presence of specific analytes, which can be gases (toluene or xylene for instance), vapours or liquids. The dye, either mixed with the core of lightguides or printed over it reacts with the analyte, resulting in a change in fluorescence. To obtain a complete sensor system, lightguides, light-source, detectors and coupling elements are integrated in a compact system. Such an optochemical sensor system enables continuous sensing and has a potential for reversibility. Additional advantages of this design are longer interaction length, possibly higher sensitivity, higher degree of integration and a future possibility for multiplexing.

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2. OPTOCHEMICAL SENSOR ARCHITECTURE

The sensor principle relies on fluorescence, where a fluorescent dye absorbs light in a certain wavelength range and emits in a different wavelength range as shown in Figure 1 (left). The presence of analytes alters this emission spectrum.

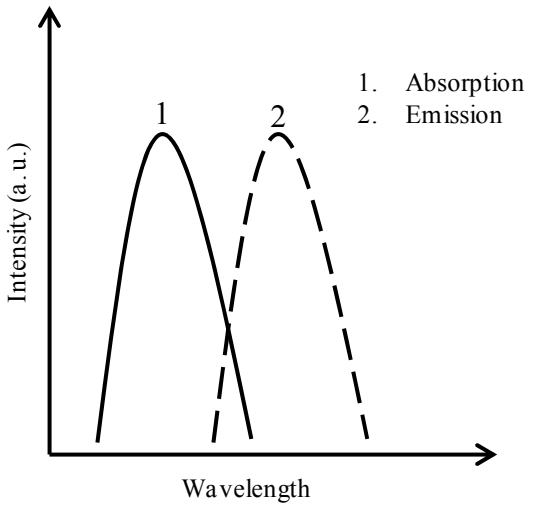

Fig.1. Possible absorption and emission spectra of a fluorescent dye.

The proposed optochemical sensor utilizes such a fluorescent dye in combination with a lightguide. In a fundamental design, as shown in Figure 2, light from a source (LED in this case) is coupled into a lightguide using a coupling element, e.g. a 45° micromirror plug[13]. The guided light interacts with the fluorescent dye and it is detected at the detector-end using a photodiode in combination with an optical filter. All these components are embedded in a foil substrate which not only acts as a cladding for lightguiding but also gives advantage of flexibility to the sensor.

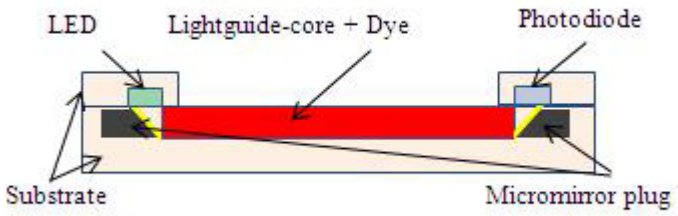

Fig. 2. Basic design of optochemical sensor with light source, lightguides, detector and coupling elements

The fluorescent dye is either mixed with the polymer used to fabricate the lightguide or printed on the top of a fabricated lightguide. In the latter situation, which is the case for silsesquioxane-based polymer lightguides, the interaction of guided light and dye occurs by means of the evanescent field. The main advantage in using optical silicones as lightguide material is the possibility of mixing the dye uniformly throughout the entire volume of the lightguide. Owing to the inherent porosity of PDMS material, gas can diffuse inside and influence fluorescence which can be detected by monitoring light propagation in the lightguide. The design also offers a possibility of having an array of lightguides with different dyes specific to various analytes which enables multi-analyte detection and holds plenty of promise in applications of gas sensing as in medicine, food packaging industry, security systems and a multitude of other areas. The mechanical flexibility of the sensor enables the use of these sensors inside gas pipes enabling detection of leakage and also ideas for integrating them with protective clothing.

3. LIGHTGUIDES FABRICATION

3.1 Polymer materials and adopted fabrication techniques

The lightguides employed in the sensor design are fabricated using two different technologies: photolithography in the case of silsesquioxane-based polymer LightLink™ and soft-lithography based replication techniques followed by capillary filling for poly(dimethylsiloxane) (PDMS) based polymers like Dow Corning®OE-6520 and LS-6257 (Nusil). While the specific core and cladding materials available for LightLink™ are used in photolithography, Sylgard®184 is used as cladding for the PDMS-lightguides. For the LightLink™ based waveguides patterned using lithography, the dye would be applied on top of the waveguide core, while for the PDMS based waveguides, the dye can also be mixed with the PDMS serving as the waveguide core.

3.2 Photolithography

Two approaches for photolithographically patterning lightguides are explored. In the first approach, LightLink™ cladding is spin-coated on a polymer-foil substrate (PET/PEN) at 200 rpm to have a uniform undercladding layer of 50µm thickness. This layer is pre-baked for 20 minutes at 90º, UV exposed for 40s and hard-baked for 10 minutes at 90º to fully cure the material. On top of the undercladding layer after hard-bake, LightLink™ core is spin-coated at 200 rpm to obtain a thickness of 50µm. This is then baked for 30 minutes at 90º on a hotplate to remove the solvents (prebake) resulting in a dry layer enabling contact lithography. A photomask is placed on top of the dried core layer, followed by UV exposure using a mask aligner MG1410 for 20s. Since LightLink™ is a negative photoresist, the parts exposed to UV light undergo partial cross-linking of the polymer. This is then subjected to baking for 3 minutes at 90º (post-exposure bake). The next step is placing the sample in a bath of dedicated developer solution XP-3636, which dissolves the spin-coated layer except the part which is UV-exposed. This followed by proper rinsing in DI water gives well defined features. As the last step, the sample is hard-baked in a convection oven for 90 minutes at 120º to realize the final cross-linking.

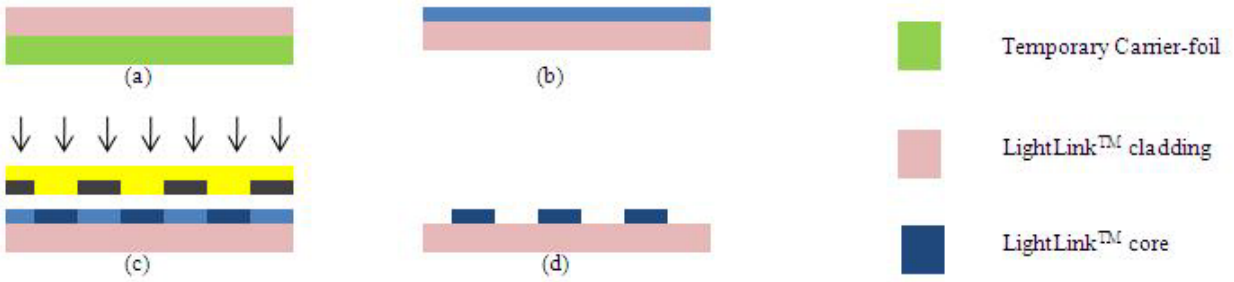

Fig 3. Process-flow of photolithography employed for fabricating free-standing LightLink™ lightguides

In a second approach, the PEN/PET is replaced by a Mylar foil (DuPont Teijin Films ™) which acts as a temporary carrier-foil on which the undercladding layer is deposited. This method is demonstrated with the specific process-flow in Figure 3. Three layers of undercladding are realized on top of the carrier-foil by repeating the steps of spin-coating, prebake and UV exposure and is then hard-baked in the convection oven to have a thick layer of LightLink™ cladding (a). After hard-bake due to poor adhesion with the Mylar foil, the undercladding layer is peeled off from the carrier-foil and is further used for defining waveguides by spin-coating (b) and pre-bake followed by UV-exposure with mask-aligner (c). The lightguides defined after developing (d) are of different dimensions in accordance with the mask used. The thickness of the lightguides depends on the spin-coating speed and a 50µm thickness was chosen. Several waveguide widths like 50µm, 100µm, 300µm, 500µm and 1mm are realized by the choice of mask.

3.3 Soft-lithography followed by capillary filling

For PDMS lightguides, an approach based on "micromolding in capillaries (MIMIC)" as a fabrication technology involving soft-lithography[14] is employed. Using capillary forces, small channels are filled with liquid polymer materials and subsequently (thermally) cured. This technique is illustrated in Figure 4.

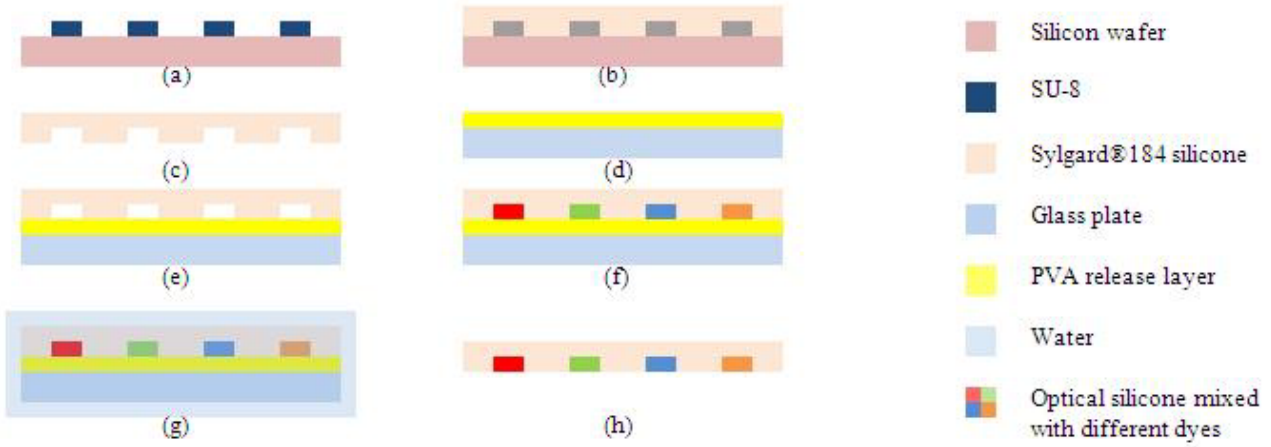

Fig. 4. Process-flow for patterning PDMS lightguides based on micromolding in capillaries.

The master mould of SU-8 3050 structures of 50µm thickness on silicon wafer is pattered by photolithography (a). Sylgard®184 is poured on the master mould (b) and this layer is thermally cured on a hotplate at 100º for 10 minutes. The cured layer is peeled off carefully from the master mould (c). A layer of PVA is spin-coated as release layer on a glass plate (d). The glass plate with PVA layer facing upward and the peeled-off silicone-layer with channels facing upward are treated using air plasma (Diener Pico system, 0.8 mbar, 24s, 190W, 40kHz generator) and they are bonded together without applying pressure (e). Several solutions of mixtures of different dyes with optical silicones like Dow Corning®OE-6520 and LS-6257 (Nusil) are prepared. Drops of each of them are applied at the channel inlet, and after waiting for some time, it is observed that these materials fill the channels due to the capillary action (f). The substrate with filled channels is cured for 14 hours at 80°C in the oven. The entire stack is then put in a water-bath to dissolve the PVA-layer (g) and flexible foils of different dye-mixed lightguides are obtained (h).

4. EXPERIMENTAL RESULTS AND DISCUSSION

The refractive indices of LightLink™ core and cladding were measured over a range of wavelengths to verify waveguiding capabilities. In a next step, the optical lightguides were characterized determining the values of attenuation at a specific wavelength, which is a measure of lightguide quality and is mainly dependent on design and fabrication. Propagation losses of LightLink™ and LS-6257 50 x 50 µm^2 lightguides were determined at 850nm, although intrinsic material absorption only contributes to a part of the total attenuation. Scattering losses and losses that arise from surface roughness and voids also add to the total loss. Therefore, the linear attenuation coefficient which is typically expressed in dB/cm, taking into account all these effects, is a good measure of lightguide quality. Additionally, transmission measurements were performed using a white-light source and a spectrometer to obtain get an idea of the wavelength specific losses. This, in future, can aid in the choice of different dyes, as the curves are obtained over the entire visible spectrum. This section also describes the measurements related to fluorescence and auto-fluorescence.

4.1 Refractive indices

The refractive indices of LightLink™ core, LightLink™ cladding materials were measured using ellipsometric method. LightLink™ cladding material is used as an undercladding layer even for lightguides on PEN/PET foils because large amount of anisotropy was observed in both PEN and PET foils in refractive index between x, y and z directions. These are shown in Figure 5. With the use of undercladding layer a refractive index variation of around 0.025 is achieved at almost all the wavelengths.

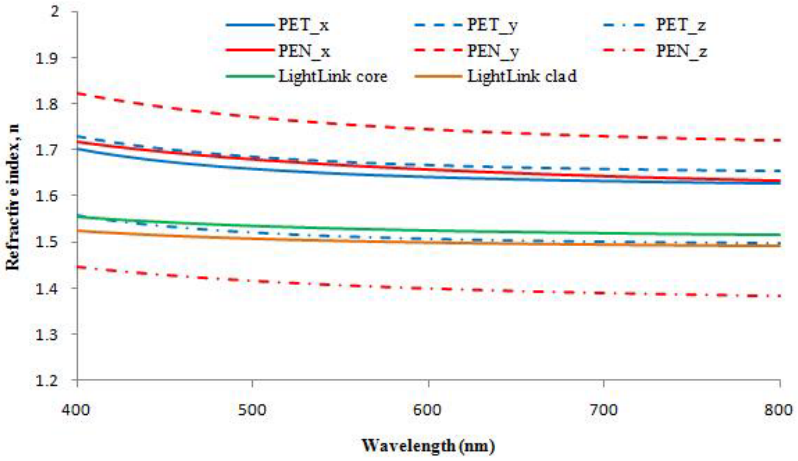

Fig. 5. Plots of wavelength specific refractive indices of PET, PEN, LightLink™ core and cladding obtained by ellipsometric technique

The refractive indices for Sylgard®184, OE-6520 and LS-6257 were measured using an Abbe refractometer in Cleanroom conditions (21±1°C, 50±10%RH) and are summarized in table 1. Also, the curing conditions are mentioned since it was observed that these slightly influence the final refractive index of the material after cross-linking[15, 16].

Table 1. Refractive index n (at 589 nm) of different optical PDMS types, measured using an Abbe refractometer (21°C)

Material	n (21°C)	PDMS curing conditions
Sylgard®184	1.413	hotplate: 2 hours at 60°C
LS-6257	1.571	oven: 14 hours at 80°C
OE-6520	1.549	oven: 14 hours at 80°C

4.2 Propagation losses

In cut-back measurements, the propagation loss (at 850nm) is calculated by comparing total attenuation for different waveguide lengths. This technique has two uncertain factors, the irreproducibility of waveguide facet and fiber-coupling.

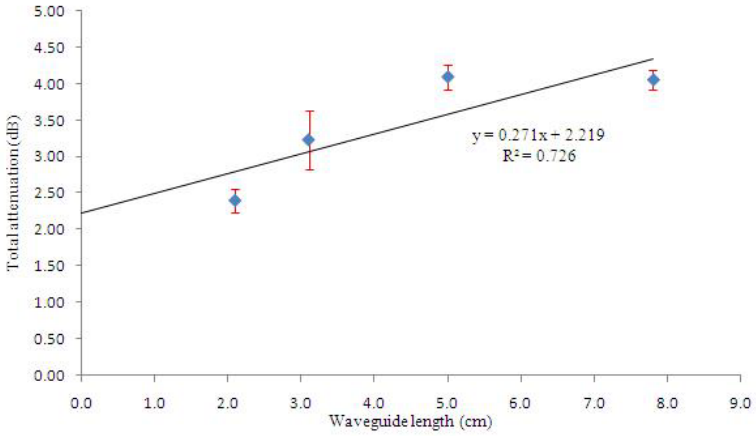

Fig. 6. Optical attenuation of LightLink™ lightguides fabricated with photolithography

In the case of LightLink^{TM} waveguides, facets are prepared by breakage of the flexible foil by bending it to an extensive bending radius of 1mm. The result of these cut-back measurements on a set of 10 waveguides is shown in Figure 6 and an associated propagation loss of 0.27dB/cm was found.

The samples with PDMS waveguides of several centimeters long was progressively cut-back in 1cm increments using a 125µm thin razor blade to make an end-facet of the PDMS sample. The results on a set of 10 waveguides are shown in Figure 7. A propagation loss of 0.14dB/cm was obtained.

Both for the Lightlink^{TM} based waveguides and the PDMS based waveguides, owing to the difficulty in obtaining reproducible facets, there is a certain variation on the measured results.

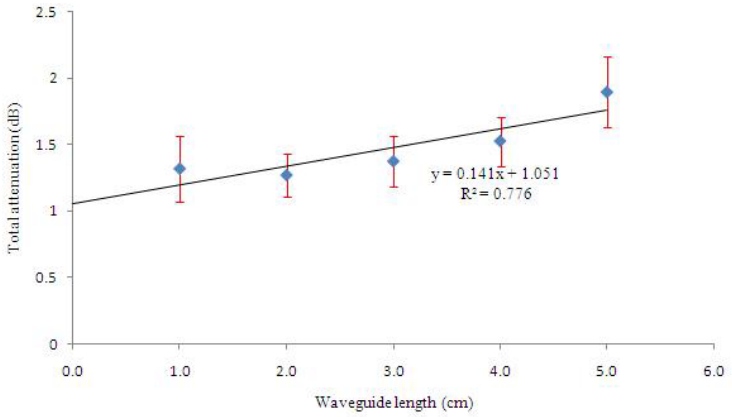

Fig. 7. Optical attenuation of PDMS lightguides based on LS-6257 core and Sylgard®184 cladding

4.3 Spectral characterisation

A Xenon lamp was used as a white light source to couple light with a collimator into a 50 µm fiber which was aligned with the help of a measurement set-up and cameras to the end-facets of 3cm long 50 x 50µm^2 PDMS lightguides. Another 50 µm fiber was used at the other end-facet to collect the light to be sent to a spectrometer to obtain the spectra through the lightguides. Also the spectrum was measured with two fibers directly in contact without the PDMS lightguides. These spectra are shown in Figure 8.

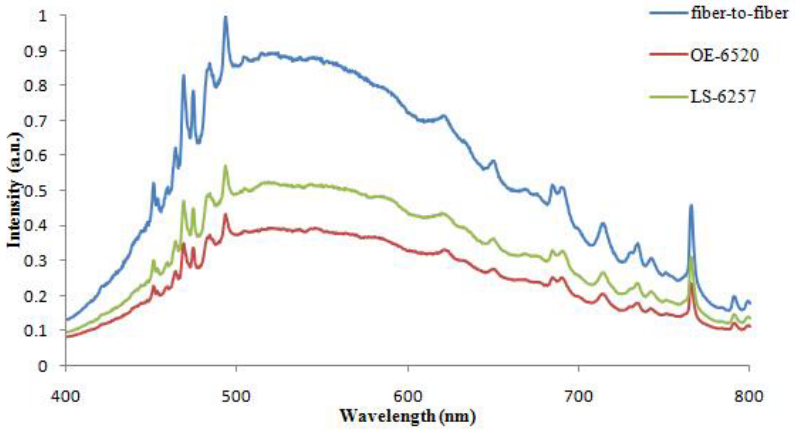

Fig. 8. Optical Spectra of PDMS lightguides based on OE-6520 and LS-6257 as core and Sylgard®184 cladding

The LS-6257 sample was found to have more attenuation inside the lightguide than OE-6520, although alignment tolerance and end-facet quality can also affect this measurement.

4.4 Fluorescence and Auto-fluorescence

Fluorescence and auto-fluorescence measurements were performed to evaluate the sensing potentials of PDMS and LightLink™ lightguides. As a proof-of-principle sensor test, some of the PDMS waveguides were mixed with a pre-mixed solution of Nile Red dye and observed under fluorescence microscope. Nile Red has an excitation in green light and emission in red. In figure 9, the bright-field images are to the left side and their corresponding images illuminated with green light are on the right. The first set of waveguides (a,b) contains 0.2% of the Nile Red solution added to LS-6257, 50 x 50µm^2 waveguides, and those were clearly visible as red. The second sample (c, d) where LS-6257 was not mixed with dye gave a dark image with no fluorescence as expected. Similarly, 500 x 50 µm^2 lightguides with 0.2% of Nile Red solution mixed with LS-6257 (e,f) gave red fluorescence while those without dye mixed (g,h) gave no fluorescence.

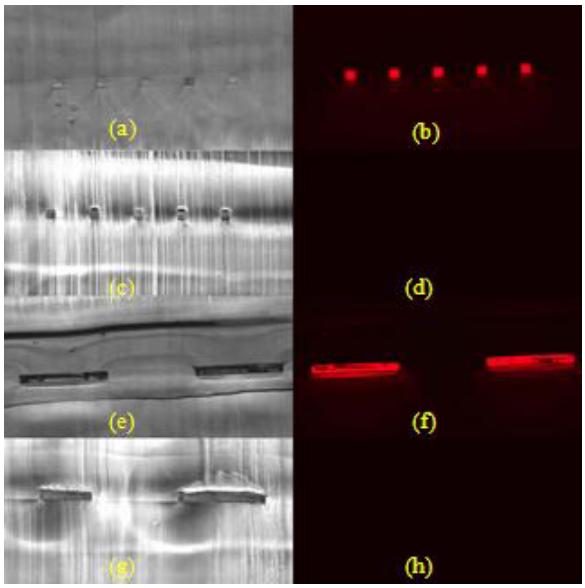

Fig. 9. Fluorescence microscopy images of dye-mixed and non-mixed LS-6257 lightguides, brightfield to the left

Varying concentrations of Nile Red solutions were mixed with OE-6520 and the corresponding emission spectra were obtained using a spectro-fluorometer exciting at 485nm. Figure 10 shows this variation corresponding to the concentration of dye.

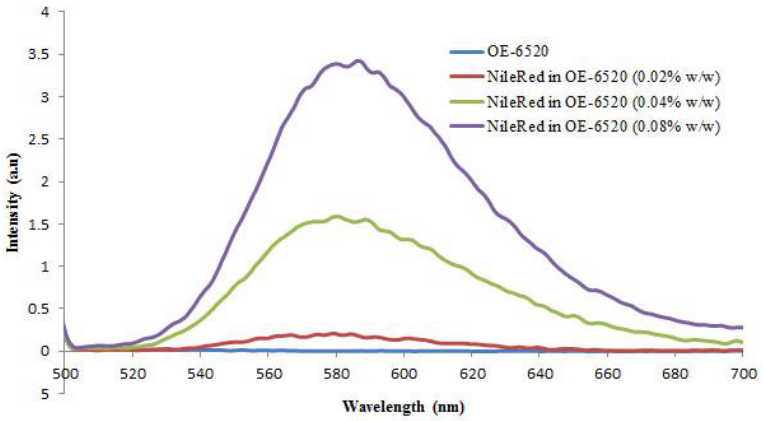

Fig. 10. Fluorescence emissions depending on concentration of Nile Red dye as obtained using spectro-fluorometer

It was also observed that LightLink™ showed auto-fluorescence in visible spectrum which could interfere with the fluorescence of dyes, while PDMS materials were found to have very little auto-fluorescence. This is shown in Figure 11 (the curve has been interpolated from 520-600 nm to eliminate the peak of excitation second harmonic).

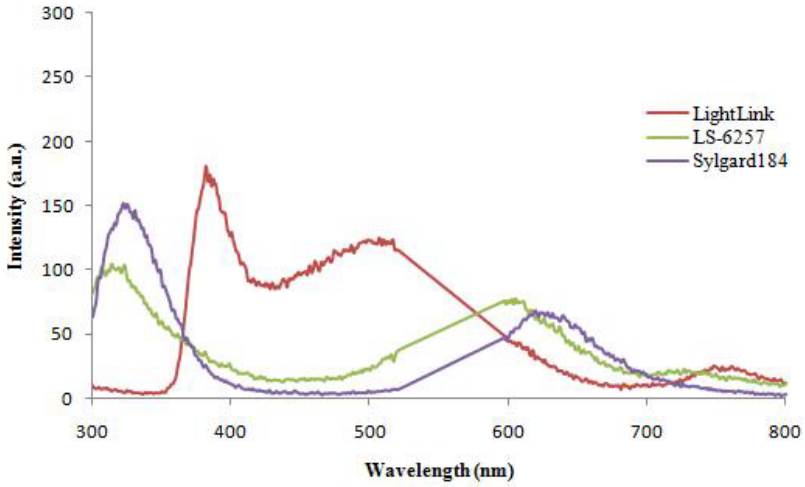

Fig. 11. Auto-fluorescence curves for LightLink™, LS-6257 and Sylgard®184

This is an advantage of using PDMS material, as in that case the sensor will be highly sensitive to the dye material itself and not to the optical material of the waveguide core, resulting in a good signal to noise ratio.

5. FUTURE OUTLOOK

Several other approaches can be adopted for in- and out-coupling other than the use of micromirrors[13]. Since PDMS materials are best-suited for moulding, imprinting of microprisms has many possibilities yet to explore. Owing to the high absorption coefficients in the UV-region, PDMS materials like LS-6946 (as shown in figure 12) and LS-6257 have promise in laser-ablation using a KrF Excimer laser. This type of laser is commonly used for polymer micropatterning and has potential of defining accurate and fine structures[17].

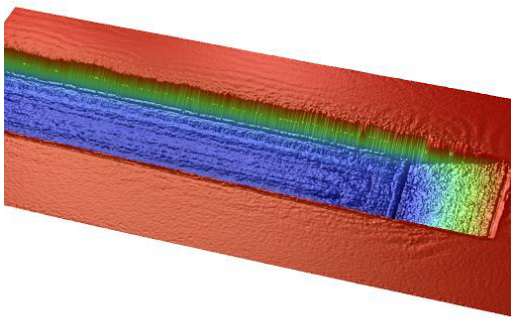

Fig. 12. Preliminary test for laser-ablating LS-6946 PDMS using KrF Excimer laser (248nm): optical profiler scan of an ablated 200µm wide and 8µm deep groove.

6. CONCLUSIONS

A foil-based optical technology platform has been proposed in realizing a multi-analyte sensor based on lightguides mixed with fluorescent dye, with many advantages over existing technologies. Two methods have been investigated for the fabrication of lightguides that form the sensing part of the optochemical sensor. Propagation losses of 0.27dB/cm and 0.14dB/cm were determined for LightLink^{TM} and LS-6257 50 x 50 μm^2 waveguides respectively. PDMS lightguides have been demonstrated to have high potential because it enables mixing of fluorescent dyes in the core of the lightguide thereby enabling easy detection of analytes, porosity, low-losses and almost negligible auto-fluorescence.

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