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Real Time Chemical Detection Using Species Selective Thin Films and Waveguide Zeeman Interferometry

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ABSTRACT

We present a chemical sensor scheme based on selective sensing surfaces and highly sensitive integrated optical transduction methods. Using self-assembly techniques, species selective thin-films are covalently attached to the surface of Si_3N_4 channel waveguides to produce robust sensor elements. Exposure to targeted analytes results in the selective absorption of these molecules onto the waveguide surface causing a change in the effective index of the guided modes. These relative changes in effective index between TE and TM modes are precisely measured using Zeeman interferometry. Our measurements demonstrate reversible, real time sensing of volatile organic compounds at ppm levels.

Keywords: chemical sensors, evanescent field sensing, waveguide interferometry

1.0 INTRODUCTION

There is an increasing need for gas sensors which can distinguish extremely low levels of particular chemicals in the presence of large concentrations of interfering species. Our goal is to develop chemical sensor arrays that are highly selective and sensitive by coupling species specific thin films with optical transduction methods. In our sensor approach, specificity is based on guest-host chemistry for molecular recognition where we design cavity shaped molecules that selectively bind targeted chemicals. These thin film reagents are covalently bound to the surface of a planar optical waveguide. Changes in refractive index caused by the selective absorption and desorption of molecules on the waveguide surface are detected by the evanescent field resulting in a change of the effective refractive index of the guided light modes propagating through the waveguide. Heterodyne detection allows us to measure these changes with high precision.

In this paper, we describe our sensor approach and present results obtained with preliminary Si_3N_4 planar waveguide structures. We also detail waveguide modifications and optimization parameters which will allow us to increase sensor sensitivity.

2.0 EXPERIMENTAL METHODS

2.1. Species Selective Thin Films

Surface self assembly techniques provide a convenient route to covalently bond host reagents on to a transducer surface to form dense monolayer or multilayer reagents with minimal sites for non-specific binding. Species selectivity is optimized by designing host reagents (cyclodextrins and calixarenes) that form guest-host inclusion complexes with the molecules to be sensed. As shown by Fig. 1, these materials are "bucket " like in structure as they possess hydrophobic cavities that are known to accommodate small molecules. In effect, these host reagents act as enzyme mimics with guest-host binding affinities that can be specifically tuned. By adjusting the size of the cavity and the chemical functionality of the bucket rims we are able to obtain highly specific recognition for selected molecules. Because these guest-host interactions are reversible and the films very thin, molecules are quickly absorbed and desorbed from the transducer surface enabling real-time sensing of chemical agents.

The selective thin film used in this study is a highly uniform, dense monolayer film where cyclodextrin (CD) reagents are covalently attached onto the surface of a reactive self-assembled monolayer (SAM). Details of the synthesis route used to prepare these monolayer reagents are detailed in Reference [1]. We have also been successful in preparing multilayer films using a variety of techniques [2,3]. The most successful of these is to covalently attach the CD and CA reagents to a polymer backbone which is, in turn, attached to a reactive SAM bonded to the surface of the transducer [4].

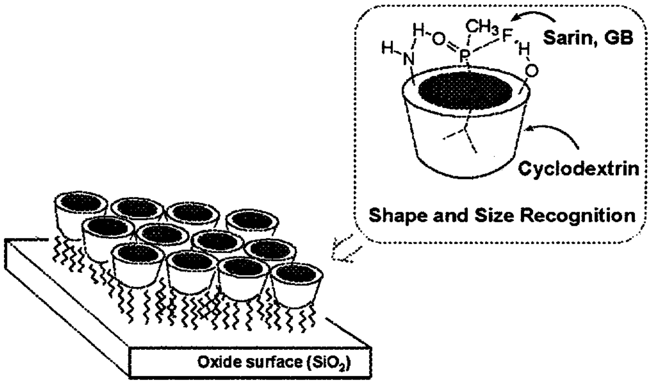

Figure 1. Species selective thin films covalently bound to a transducer surface.

2.2. Si_3N_4 Waveguides

For our sensing elements we use Si_3N_4 channel waveguides coated with the species selective reagents described above. The rib waveguide structure used in our interferometer is illustrated in Fig 2. Using a low pressure chemical vapor deposition (LPCVD) a 300 nm thick Si_3N_4 (n=2.00) film was deposited on a 3um thick SiO2 (n=1.46) buffer layer. Rib waveguides with different widths were formed by etching 25 nm high mesa structures into the Si_3N_4 film. To facilitate the attachment of chemically sensitive films, a thin (approximately 20nm) top silica layer was deposited using plasma enhanced chemical vapor deposition (PECVD). Our sensor scheme relies on the interaction of the evanescent field with a selective surface layer. The evanescent field interacts only over a short distance close to the surface of the waveguide and decays exponentially away from the interface. As a result, well confined modes offer higher sensitivity to changes in the optical characteristics of the surface layer. Because they feature tight vertical mode confinement (see Fig. 3), very thin high refractive index Si_3N_4 films are well suited for our sensor applications. Si_3N_4 also exhibits low optical transmission losses allowing for long sensor interaction lengths to increase sensor sensitivity. Moreover, the fabrication of Si_3N_4 waveguides is fully compatible with conventional microelectronics processing techniques allowing for ease of mass manufacturing.

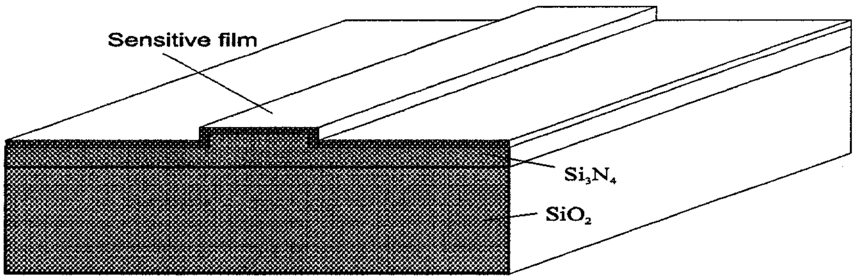

Figure 2. Si_3N_4 rib waveguide.

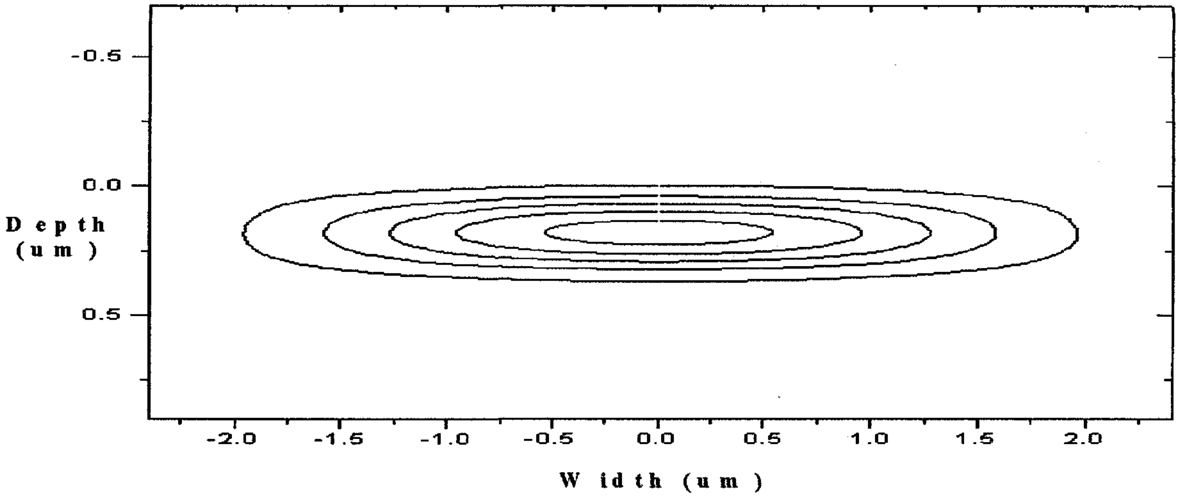

Figure 3. Optical power distribution for Si_3N_4 rib waveguide of Fig. 2. The top of the sensitive layer is at a depth of 0um.

2.3 Waveguide Zeeman Interferometry

Our sensor instrument (see Fig. 4) is a polarimetric interferometer based on the principles outlined in Reference [5]. We essentially use the orthogonal polarized beams (TE and TM modes) generated by a split frequency Zeeman gas laser as two arms of an interferometer. These two modes differ by only 3.3×10^{-7} nm in wavelength with a difference frequency of 250kHz. As the two modes propagate through the waveguide they interact with the sensitive layer and experience different changes in effective refractive index (Δ_{TM} and Δ_{TE}). Light from the output of the waveguide is passed through an analyzing polarizer with it's transmission axis at 45°. The two laser lines interfere at the detector producing a beat frequency of 250kHz. The phase of this beat frequency depends on the differences in effective index seen by each mode. This phase difference $\Delta\phi$ is

$$\Delta\phi = 2\pi / \lambda o \, (\Delta_{TM} - \Delta_{TE}) \, L \tag{1}$$

Where $\lambda = 632.8$nm, Δ_{TE} and Δ_{TM} are the changes in effective refractive index of the two guided modes due to the selective surface binding events and L is the sensor interaction length. The phase of this 250kHz sinewave signal is measured relative to the 250KHz reference signal generated by the Zeeman laser.

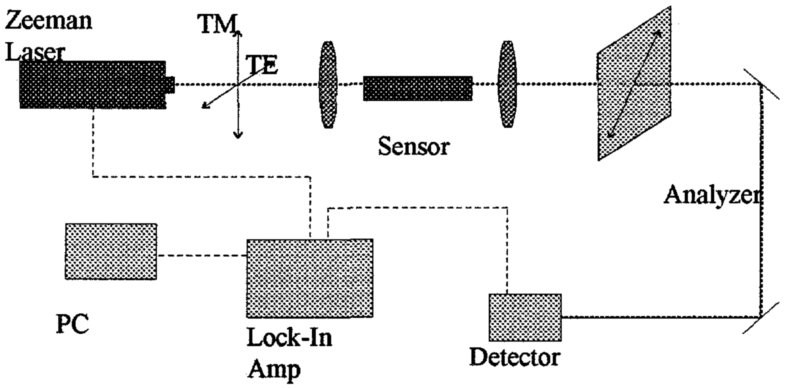

Figure 4. Schematic diagram of measurement setup.

As expressed in Eq. (1), sensor sensitivity can be increased by maximizing the differences in effective refractive index (Δ_{TE} -Δ_{TM}) due to exposure to targeted chemicals and by increasing the sensor path length (L). Using a finite difference method we can calculate an optical sensitivity constant [5] , dNeff/dnS , which describes the change in the effective refractive index as the refractive index of the sensitive layer changes. Calculated sensitivity constants for TE and TM modes as a function of Si_3N_4 waveguide thickness are illustrated in Fig. 5. The individual sensitivity constants are proportional to the intensity of the evanescent field within the sensitive layer. Further details on our waveguide modeling methods and approximations will be described in Reference 6. Our current experiments use unoptimized waveguide structures with a thickness of 300nm. From Fig 5, we conclude that by using waveguides with a thickness of 190nm we can maximize the difference between the sensitivity constants of the two modes and gain a factor of two increase our sensor sensitivity.

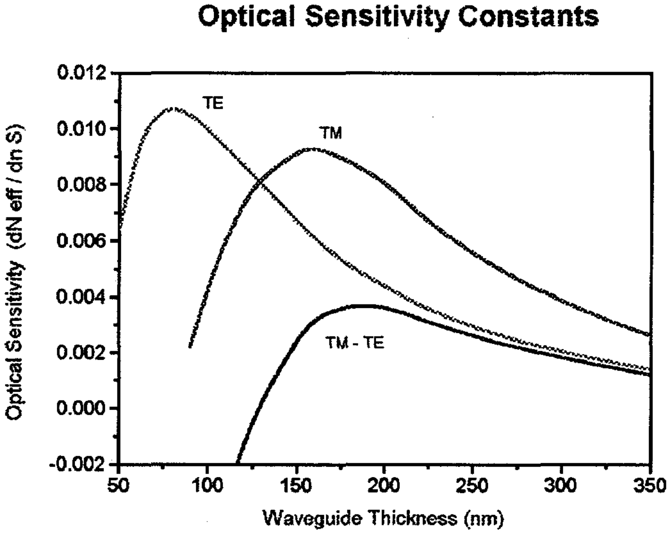

Figure 5. Calculated optical sensitivity constants for TE and TM modes as a function of Si_3N_4 layer thickness.

3.0 RESULTS AND DISCUSSION

Figure 6 shows the interferometer's phase response when exposed to several different concentrations of toluene in air. The sensor shows an immediate response when toluene is introduced into the air flow system and quickly returns to baseline when toluene is removed. For 20ppm we measure a phase shift of 1.3° for a waveguide 1.5 cm in length. Using Equation 3, this corresponds to an effective index difference between the two modes of 1.1x $^{10-7}$. In Fig. 7, our sensor phase response is shown as a function of toluene concentration. The curve is partially nonlinear with lower concentrations producing a larger than expected phase response. This is interesting in that this same effect has been noted using identical species specific thin films on surface acoustic wave transducers. Future work will include measurements over a broad spectrum of concentrations to verify and further study these results. Also, in Fig. 7, we show the calculated phase change as a function of the refractive index change in the selective surface layer. Our models used for these calculations approximate the sensor with a slab waveguide structure.

We have designed new waveguide structures to improve the sensitivity of our sensors by increasing the length of the waveguide channels and optimizing the Si_3N_4 layer thickness to maximize the differential change in the effective index of TE and TM modes caused by exposure to chemical agents. These new waveguides are currently being fabricated. Because silicon nitride is a high refractive index material with low absorption losses we can design serpentine like channels with small bend radii to increase the interaction length of the channel without increasing the size of the chip. In order to compensate for temperature and other common mode effects we will also include reference channels on the same substrate. These reference channels will be coated with passivating thin films which effectively block the binding of targeted agents to the waveguide surface. Improvements in sensor sensitivity and specificity will also be addressed through the further optimization of species selective thin films for targeted chemical agents and through the use of multilayer polymer films.

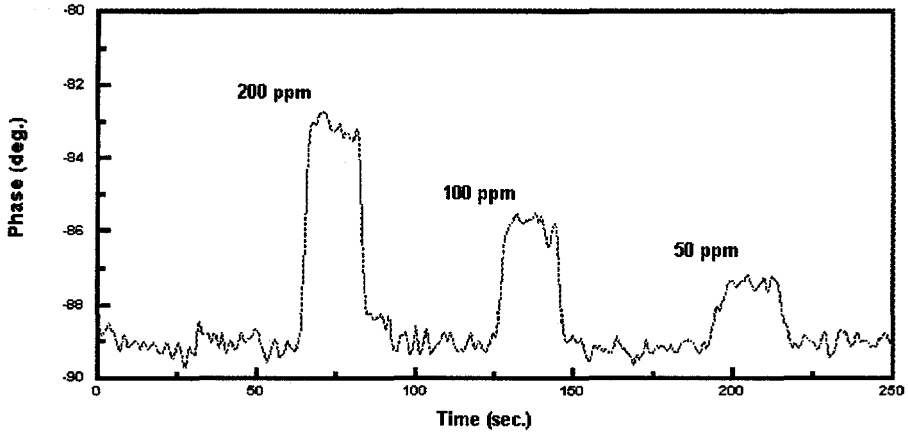

Figure 6. Sensor phase response upon exposure to three different concentrations of toluene.

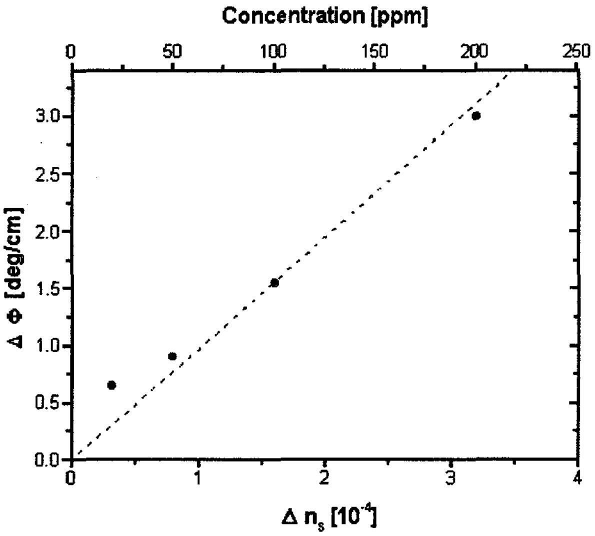

Figure 7. Interferometer phase difference per waveguide length as a function of toluene concentration (circles) and as a function of change in the refractive index of the sensitive layer (dashed line).

4.0 CONCLUSION

Using species selective reagents, Si3N4 channel waveguides and Zeeman interferometry we have demonstrated rapid and reversible sensing of volatile organic compounds. In addition to presenting our first experimental results we have outlined a strategy for the optimization of Si_3N_4 waveguide structures which will allow us to increase our sensor sensitivities considerably. The high intrinsic specificity's of our thin films combined with waveguide interferometry and sensitive heterodyne detection offer the potential for future development of compact sensor arrays which can be tailored for a variety of civilian and military chemical sensing needs.

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