

## Magneto-photonic crystal optical sensors with sensitive covers

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We report on a magneto-photonic crystal on-chip optical sensor for specific analyte detection with polypyrrole and gold nano particles as modified photonic crystal waveguide cover layers. The reaction of the active sensor material with various analytes modifies the electronic structure of the sensor layer causing changes in its refractive index and a strong transduction signal. Magneto-photonic crystal enhanced polarization rotation sensitive to the nature of the cover layer detects the index modification upon analyte adsorption. A high degree of selectivity and sensitivity are observed for aqueous ammonia and methanol with polypyrrole and for thiolated-gold- with gold-nanoparticles covers. © 2011 American Institute of Physics. [doi:10.1063/1.3633344]

The detection of toxic and oil-contaminants has attracted strong attention due to concerns over industrial emissions and other environmental hazards.<sup>1,2</sup> Many sensing techniques have been explored and reported in the literature.<sup>1-4</sup> The study of conducting polymers and metal nano materials as active layers in biological and chemical sensors has increased in recent years as these have allowed vast improvements in sensitivity, response time, and cost reduction compared to other commercially available sensor materials.<sup>1,2</sup> Among the conductive polymers, polypyrrole (PPy) is one of the most explored as the active component in many sensing techniques for the detection of toxic substances and vapors.<sup>1,2,4</sup> Similarly, the unique electronic and optical properties of gold nanoparticles (GNPs) provide excellent active layers for optical sensors for specific analyte detection.<sup>3</sup> In this study, we couple PPy and GNP active sensor materials with magneto-optically active on-chip photonic crystals (MPCs) for detection by substance adsorption in a sensor layer. A highly sensitive polarization rotation (PR) response to the MPC cover refractive index modifications is shown to detect the presence of various analytes. We employ PPy cover layers for the detection of aqueous ammonia (aq. NH<sub>3</sub>) and methanol (MeOH) while GNP cover layers are used for thiol detection. Thiols are among the most prevalent components in crude oil, and hence, our work constitutes a step towards the detection of crude oil leaks or spills.

Prior work by some of the present authors has demonstrated significant PR and sensitivity to cover-layer refractive index in waveguide MPCs for near-band-gap-edge fundamental to high-order waveguide mode backscattering.<sup>5-9</sup> Here, we make use of this strong polarization response between different mode-orders to demonstrate detection and significant sensitivity to various analytes. Easily detectable polarization changes on the order of 10° or more are observed, with ranges of rotation specific to analyte type.

The simultaneous presence of optical gyrotropy (Faraday rotation) and linear birefringence ( $n_{TE} \neq n_{TM}$ ) in magneto-

optic waveguides is responsible for these large polarization effects, as discussed in Refs. 6-9.  $n_{TE}$  is the transverse-electric and  $n_{TM}$  the transverse-magnetic mode index. Optical gyrotropy is parameterized by the parameter  $g$ . Linear birefringence is due to geometrical confinement of the optical signal in asymmetric waveguides and lattice-mismatch-induced stress on the waveguide film. Under these conditions, local elliptically polarized modes form in the guide, parameterized by

$$\hat{e}_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} \cos \alpha \pm \sin \alpha \\ \pm i \cos \alpha - i \sin \alpha \\ 0 \end{pmatrix}$$

where  $\tan(2\alpha) = \frac{n_{TE}^2 - n_{TM}^2}{2g}$  as discussed in Refs. 8 and 9. Mode coupling arising from the periodic variation in elliptical polarization and refractive indices in the magneto-photonic crystal is responsible for the large polarization effects near the stop band edges. The role of the Faraday effect consists in establishing the character of the normal modes as elliptically polarized and, as a consequence, influencing the coupling with backscattered highly birefringent modes by the photonic crystal. The rotation is due to the selective back-reflection of polarization components out of the incident fundamental waveguide modes. In other words, the enhanced PR at the stop band edges originates from the partial selective reflection of positive- and negative-helicity higher order normal modes. Opposite helicity modes possess spectrally detuned stop bands and orthogonally oriented elliptical polarization. This detuning is due to the large birefringence of the high-order backscattered modes, resulting in rotated transmitted polarization near the band edges.<sup>6,8,9</sup>

PR is here defined as the change in semi-major axis orientation of the output polarization ellipse relative to input TE polarization. This PR sensitivity to waveguide cover refractive index serves as a sensitive tool for optical sensing. Our tests show a monotonic enhancement of rotation with cover index, hence sensitivity to analyte-induced index changes, as shown in Fig. 1(c). Here, the rotation changes are produced by the changes in ellipticity of the waveguide modes and detuning of the opposite helicity stop bands due to the

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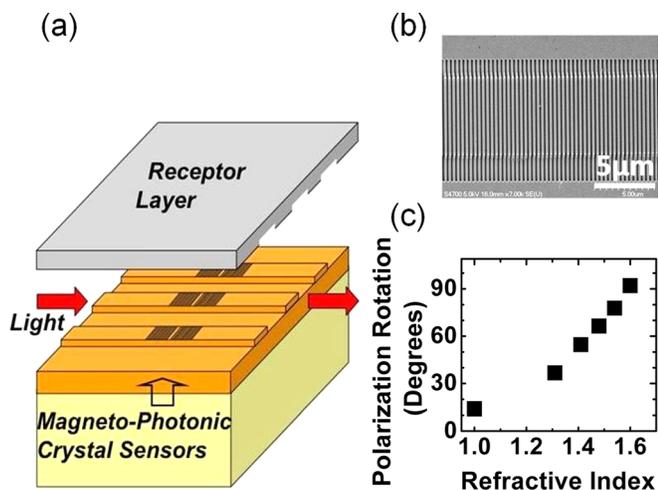


FIG. 1. (Color online) (a) Schematic representation of the MPC optical sensor with receptor layer. (b) Scanning electron micrograph of the grating region of the sensor. (c) PR versus cover index for a series of liquid analytes.

changes in waveguide mode indices upon changes in cover-layer refractive index. A complete theoretical and experimental treatment of band edge PR in MPCs was presented in earlier publications by some of the present authors.<sup>5,7-9</sup>

The study reported here explores the integration of the MPCs with active sensor layers to detect aq.  $\text{NH}_3$  and MeOH and the crude oil component thiol. Conducting polymers undergo reversible and irreversible changes in their optical properties and electrical resistance when exposed to certain toxic substances. A few of the many reasons that they qualify as excellent active layers in sensor systems are that they demonstrate high sensitivity and short response time while operational at room temperature. We employ PPy as one of the active sensor layers in our study because in addition to having all the above qualities, it can be easily synthesized and is a proven excellent detector of ammonia and other volatile organic substances.<sup>1,4</sup> Among the other sensor materials used in the field of sensor research, GNPs are also of great interest owing to their fast and direct electron transfer capability with certain analyte substances.<sup>3</sup> The sensing mechanism involves the alteration of electronic and optical properties of GNPs upon interaction with target molecules. We use GNPs in suspension as the modified cover layer. In this study, we demonstrate sensing of thiolated GNPs as an initial test for the detection of thiols present in crude oils.

The sensor consists of a ridge waveguide MPC with active sensor layer deposited on the grating. Figure 1 shows (a) a schematic depiction of the sensor, (b) a scanning electron micrograph of the grating region, and (c) the response of a typical sample to cover index changes. All waveguide MPCs used in this study were fabricated on Bi-substituted iron garnet films grown on  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  substrates by liquid phase epitaxy.  $6\ \mu\text{m}$ -wide waveguides with ridge height  $800\ \text{nm}$  were formed by standard lithography and plasma etching techniques. Grating structures,  $200\ \mu\text{m}$ -long, were patterned on the ridge waveguides by ion beam milling.

The samples used for tests with modified PPy covers were fabricated on  $2.7\ \mu\text{m}$ -thick  $\text{Bi}_{0.8}\text{Gd}_{0.2}\text{Lu}_{2.0}\text{Fe}_5\text{O}_{12}$  films with grating groove depth  $700\ \text{nm}$ . Prism coupler measurements of the refractive indices of the film slab before surface patterning for TE input fundamental, first-, and second-order modes are

$2.3030$ ,  $2.2603$ , and  $2.1882$ , respectively. Linear birefringence for the first three modes are  $0.0008$ ,  $0.0051$ , and  $0.0121$ , respectively. The specific Faraday rotation of this film is  $80^\circ/\text{mm}$ . PPy was synthesized by pyrrole monomer chemical oxidation. Vapor phase deposition with iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as oxidant solution was employed to obtain PPy cover layers on the photonic crystal (PC) samples.  $0.1\ \text{M}$  oxidant solution in acetone was deposited on the PC using an optical fiber attached to a micro-manipulator. The oxidant deposited sample was then exposed to pyrrole vapor for  $10\ \text{s}$  where the monomer solution was kept in  $60^\circ\text{C}$  water bath. Optical transmission was measured for TE input light by end-fire fiber coupling from a  $1480$ - $1580\ \text{nm}$  tunable laser source. PR of the output light was determined by measuring the Stokes vector parameters. All the optical measurements were done in a saturating magnetic field of  $300\ \text{Oe}$  applied along the waveguide axis. PR was measured before and after the PPy layer came in contact with an ultra small volume of analyte solutions. Two analytes,  $29\%$  aq.  $\text{NH}_3$  solution and laboratory grade MeOH, were tested. A significant change in PR response was observed upon exposure to both aq.  $\text{NH}_3$  and MeOH. Figures 2(a) and 2(b) show the PR output measured for PPy-deposited MPC samples before and after exposure to aq.  $\text{NH}_3$  and MeOH, respectively. The two sets of data (solid and open squares) for PPy cover shown for wavelengths below

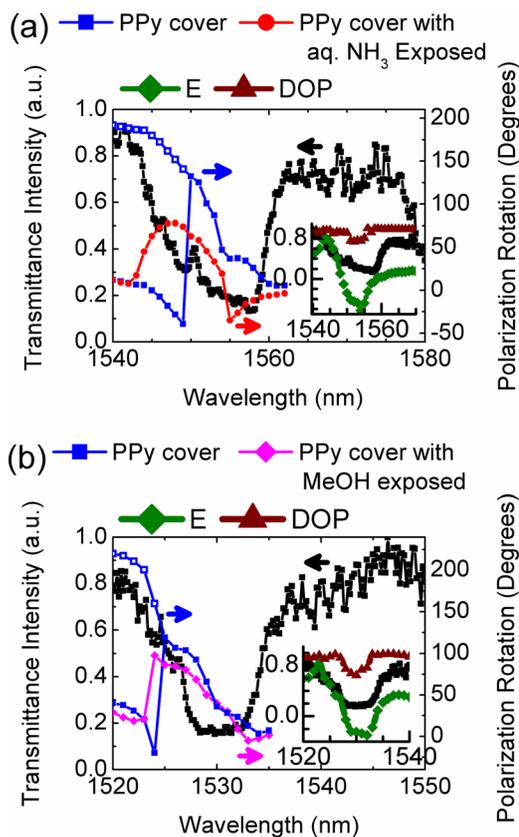


FIG. 2. (Color online) Measured transmittance (for air cover) and PR of PPy deposited PC before and after exposure to (a) aq.  $\text{NH}_3$ , with polarization transduction signal  $\sim 50^\circ$  for different samples. (b) MeOH, polarization transduction signal  $\sim 10^\circ$ , for different samples, showing consistently sensitive and easily measurable response. PR angles for both  $\theta$  (solid squares), and  $180^\circ + \theta$  (open squares) are shown for wavelengths below  $1550\ \text{nm}$  for Figure 2(a) and below  $1525\ \text{nm}$  for Figure 2(b). The insets show the degree of polarization and ellipticity for when PPy cover exposed to aq.  $\text{NH}_3$  and MeOH, respectively.

1550 nm in Fig. 2(a) and below 1525 nm in Fig. 2(b) plot rotation angles  $\theta$  and  $180^\circ + \theta$ , since they represent the same orientation of the ellipse and could be read either way. The transduction signal is estimated from angle  $\theta$ . Estimations from  $180^\circ + \theta$  yield even larger transduction signals. Tests were repeated on 3 samples each with reproducible results. Transmittance and PR measurements are done for the band gap formed by the coupling between forward propagating fundamental mode to reflected second-order mode. The deposition of PPy reduces the overall transmittance through the waveguide PC; however, the shift of the band position is limited to 1-2 nm maximum and the coupling strength to the PC remains intact.

The exposure process consists of depositing a minute drop ( $\sim 10 \mu\text{L}$ ) of liquid MeOH or ammonia on the cover layer and allowing it to dry. It is reported that PPy undergoes irreversible changes through longer exposure to a high concentration of aq.  $\text{NH}_3$ .<sup>4</sup> Our tests agree with the activation of an irreversible process showing no change in PR after a week from the first measurement done for ammonia exposed PCs. The same is true for MeOH exposed PCs. The change of PR to ammonia exposure was consistently  $\sim 50^\circ$  at the peak of the spectral response, while for MeOH it was  $\sim 10^\circ$ , for multiple samples tested. The sensor exhibits a high degree of PR selectivity between the two analytes due to the different electronic interaction of each analyte with the PPy chains. Both ammonia and MeOH are electron donating substances. When they interact with PPy, which is in a doped state by oxidation with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  becomes de-doped causing change in electrical conductivity and hence refractive index. It can be concluded that PR is highly influenced by the PPy-analyte interaction yielding high sensitivity and selectivity. Ellipsometric analysis of PPy films deposited on Si substrate supports the results obtained by PR showing a refractive index reduction of about 10% upon exposure to ammonia.

The optical tests with GNP cover layers were carried out with a 200  $\mu\text{m}$  long MPC fabricated on  $\text{Bi}_{1.28}\text{Lu}_{1.69}\text{Gd}_{0.03}\text{Fe}_{3.65}\text{Ga}_{1.35}\text{O}_{12}$  film of 348 nm period and grating groove depth 700 nm. The refractive indices of the first four waveguide modes are 2.2805, 2.2425, 2.1784, and 2.0876. Linear birefringence was measured at 0.0002, 0.0041, 0.0097, and 0.0169, respectively. The intrinsic Faraday rotation of the film is  $95^\circ/\text{mm}$ . 10 nm-diameter-gold and co-polymer-thiolated-gold nanoparticle solutions used in the tests were prepared at our laboratories. The GNPs were synthesized by citrate reduction.  $\text{HAuCl}_4$  aqueous solution was heated under vigorous stirring. Once the solution began to boil, sodium citrate solution ( $\text{Na}_3\text{Ct}$ , 26.1 mg in 5 mL deionized water) was added. This quantity afforded a molar ratio of  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  of 3.5 mol:1.0 mol. The solution was maintained at a boil for 2 h with vigorous stirring before it was allowed to cool down to room temperature. The solution continued stirring overnight at room temperature followed by a sonication treatment. Some of the GNPs were bonded to an organic block copolymer shell through a thiol end group. Block copolymer synthesis and composition is described elsewhere.<sup>10</sup> The bonding to the gold was accomplished by combining the GNP solution with the thiolated copolymer and shaking the combined solution overnight in the dark.

The waveguide cover was modified by applying a small drop of solution on the PC waveguide samples, and their

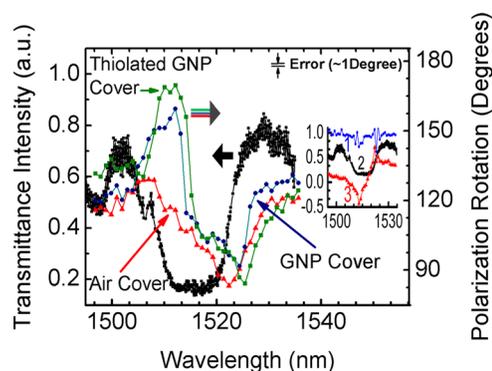


FIG. 3. (Color online) PR for fundamental to third-order backscattered mode stop bands with air, GNP and thiolated GNP as covers. In our measurements, the angle and its  $180^\circ$  complement are indistinguishable. The inset plots 1, 2, and 3 show degree of polarization, transmittance, and ellipticity for air cover, respectively.

stop bands and PR induced by the cover were measured. The gold was then removed with solvents, gold etchant, and water. The samples were re-tested to make sure the original (air cover) results were recovered. The thiolated-gold solution was then deposited and the samples optically re-tested. A distinct change in polarization of about  $10^\circ$  between the gold and thiolated-gold cover was observed, proving a definite sensitivity to co-polymer-thiol adsorption. The PR mechanism here is not due to plasmon resonances but to changes in cover index. In addition, very clear and strong stop bands persisted in the presence of the GNPs even though a gold cover absorbs some light. Figure 3 shows the experimentally measured transmittance and PRs for air, gold, and thiolated gold covers for the band gap formed by forward propagating fundamental to reflected third-order mode.

In summary, we have developed an optical sensing technique for the detection of toxic substances. Active sensor layers PPy and GNPs were employed as the modified cover layers in MPC devices. The PR change upon analyte adsorption was used as transduction signal. Detection of aq.  $\text{NH}_3$  and MeOH were demonstrated with high degree of selectivity with PPy as the modified cover layer of the MPC sensor. Sensor sensitivity and selectivity can be further improved by increasing the doping level of PPy. GNP modified-MPCs were used to demonstrate a distinct change in PR for gold and thiolated gold covers. Thus, a sensitive technique was developed for possible application in crude oil detection.

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