Porosity Waveguide in the Kretschmann Configuration for Small Molecule Detection

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ABSTRACT
In this work, we theoretically and experimentally demonstrate a highly sensitive porous silicon membrane waveguide biosensor in the Kretschmann configuration, and show how the cladding material directly impacts the waveguide sensor detection sensitivity and resonance width. Dielectric and metal-clad porous waveguides in the Kretschmann configuration have the potential to achieve significantly enhanced performance for small molecule detection compared to planar waveguide and surface plasmon resonance sensors due to increased surface area and strong field confinement in the porous waveguide layer. First order perturbation theory calculations predict that the quality factors of polymer-cladded porous silicon waveguides with porous silicon losses less than ~500 dB/cm are at least two times larger than the quality factors of gold-cladded porous silicon waveguides and traditional surface plasmon resonance sensors.

Keywords: Porous silicon, waveguide, sensitivity, Kretschmann, quality factor, perturbation theory, surface plasmon resonance, sensor

1. INTRODUCTION
Surface plasmon resonance (SPR) sensors in the Kretschmann configuration are considered to be the state-of-the-art label-free technology for studying biomolecular interactions [1]. However, for the detection of very small molecules, SPR sensors are challenged due to their limited surface area. Only a finite number of molecules can attach to the metal surface of SPR sensors; if the refractive index change induced by the presence of these molecules is below the resolution of the sensor, then the molecules cannot be detected. Recently, porous dielectric materials have attracted much attention for small molecule detection due to their larger available surface area for molecule binding. The large internal surface area of nanoscale porous materials enables a greater number of molecules to interact with the electric field and contribute to the effective refractive index change experienced by the sensor. Metal-cladded porous dielectric waveguides in the Kretschmann configuration have been reported for improved molecular detection sensitivity compared to traditional SPR sensors. These metal-cladded waveguide sensors are in essence SPR sensors with an added porous dielectric layer. Porous waveguides utilize the interaction of guided waves with biomolecules to transduce a sensor response in contrast to SPR sensors that employ an evanescent wave-based detection approach. Gold-cladded porous silica [2], porous titania [3], and porous alumina [4] waveguide sensors have been demonstrated for the detection of biotin-streptavidin binding, myoglobin adsorption, and bovine serum albumin adsorption, respectively.

Among porous materials, porous silicon (PSi) is an excellent candidate for sensing applications, in part due to the large range of achievable pore sizes and established protocols for surface functionalization [5, 6]. The pore size, as well as porosity and film thickness, can be precisely controlled by adjusting the electrochemical etching conditions and silicon substrate doping. Porous silicon films have been demonstrated for the detection of a variety of biomolecules, including DNA, viruses, and proteins [7]. Recent experiments have revealed a size dependent sensitivity for porous silicon sensors such that there exists an optimal pore size for the most sensitive detection of a given sized biomolecule [8].

In this work, we seek to combine the advantages of the metal-cladded porous waveguides and porous silicon material system. Building on our very recent demonstration of polymer-cladded porous silicon waveguides in the Kretschmann configuration for DNA detection [9], we provide a theoretically analysis of the influence of various polymer cladding and porous silicon layer parameters on the detection sensitivity of these sensors. We also consider metal-cladded porous silicon waveguides, and compare our calculations to experimental measurements.

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2. DESCRIPTION OF MULTILAYER WAVEGUIDE STRUCTURE

2.1 Porous silicon membrane waveguide schematic

Figure 1 shows the schematic for the PSi membrane waveguide with two possible cladding materials: polymer or gold. The low index polymer or gold layer (cladding layer, \(\varepsilon_2\)) is deposited directly onto a high index prism (\(\varepsilon_1\)). Alternatively, the cladding layer could be deposited on a glass slide that is index matched to the prism. Any gap between the glass slide and prism would be filled with an index matching solution. A PSi membrane with dielectric constant \(\varepsilon_3\) is deposited on top of the cladding layer, acting as the waveguide layer or core layer. For our theoretical calculations, we consider the semi-infinite medium on the opposite side of the PSi layer to be air; however, when the sensor is used with a microfluidics flow cell, the medium could be water or a buffer solution.

Light is coupled into the PSi layer via a cubic zirconia prism with refractive index \(n_1=2.1252\) at wavelength of \(\lambda=1550\) nm. We consider transverse-electric (TE) polarized light in this work, although PSi waveguides also support transverse-magnetic (TM) modes. At resonant angles, \(\theta\), the tangential component of the incident wave vector in the prism matches the wave number of a guided mode, allowing light to be coupled and propagate in the PSi layer (\(x\)-direction). The electric field is confined inside the PSi layer under these conditions, and it decays rapidly along the \(z\) and \(-z\) directions in the polymer/gold and air cladding layers, respectively. Resonant angles are identified as dips in the attenuated total reflectance (ATR) spectrum. Since molecules infiltrated into the PSi layer change the effective index and propagation constant of guided modes, the presence of molecules in the pores is detected by observing an angular shift of the resonance dips in the ATR spectrum, as demonstrated in section 4.

![Fig. 1. Schematic diagram of polymer- or gold-cladded PSi waveguide sensor. A prism is used to couple the light into the PSi waveguide layer at particular resonant angles via an evanescent wave through the cladding. Waveguide modes are confined in the porous silicon layer due to total internal reflection at the interfaces with the lower index cladding materials.](image)

2.2 Fabrication and characterization of porous silicon membrane waveguide

Porous silicon formation by electrochemical etching is a well-characterized procedure [5]. In this work, we use an n-type silicon wafer (<100>, 0.01 \(\Omega\cdot\text{cm}\)) and an electrolyte of 5.5 % aqueous hydrofluoric acid. Two different current densities were applied to two different samples to create \(~1\) \(\mu\)m thick porous silicon layers on the silicon substrates. A current density of 40 mA/cm\(^2\) was applied for 35 seconds to form a lower porosity film on one sample and a current density of 57 mA/cm\(^2\) was applied for 25 seconds to form a higher porosity film on a second sample. The PSi films were removed from their respective substrates by applying several high current density pulses (250 mA/cm\(^2\)) that allowed the porous films to detach from the substrates. In order to attach the PSi film to the cladding layer and multilayer waveguide structure shown in Fig. 1, 0.25% formvar polymer in ethylene dichloride (Ernest F. Fullam, Inc.) was dropped onto the surface of a cubic zirconia prism and the porous silicon membrane was carefully placed on top of the polymer solution [9]. Once the ethylene dichloride evaporated, a thin film of formvar (\(n\sim1.5\), transparent in infrared region) remained between the PSi layer and the prism. The thickness of the polymer layer was controlled by the percent loading of the polymer in the solvent.
Figure 2 shows the waveguide modes measured using ATR. The PSi film formed at 40 mA/cm$^2$ for 35 seconds gives rise to the guided mode near 55° while the PSi film formed at 57 mA/cm$^2$ for 25 seconds gives rise to the waveguide resonance near 60°. We note that examination of the electric field distributions indicated that the mode near 55° is a 1$^{st}$ order mode while the mode near 60° is a 0$^{th}$ order mode. We note that examination of the electric field distributions indicated that the mode near 55° is a 1$^{st}$ order mode while the mode near 60° is a 0$^{th}$ order mode. In order to determine the exact refractive index of the PSi films, thicknesses of the polymer layers, and losses associated with the PSi waveguide, the experimental results were matched with the theoretical calculations [10]. First, the optical thicknesses of the PSi and polymer were determined by matching the resonance angle position. Next, PSi absorption and scattering losses were included by allowing the imaginary part of the silicon dielectric constant at 1550 nm to vary until the full-width-at-half-maximum (FWHM) of the resonances were matched. After optimization, we found a very good fitting to be given by the following values: $d_2=0.8$ μm, $n_2=1.5$, $d_3=0.98$ μm, and PSi porosity=56% for the mode near 55°, and $d_2=0.66$ μm, $n_2=1.5$, $d_3=0.98$ μm, and PSi porosity=65% for the mode near 60°. For both cases, the imaginary part of the refractive index of the silicon wafer was set to 0.03 to match the experimental FWHM. This value is much larger than anticipated from absorption losses; the dominant contribution is from scattering losses caused by the rough interface after lifting-off the PSi membrane from the silicon substrate. Typical PSi losses are expected to be in the range of 0.00001 to 0.0005 for the imaginary part of the silicon refractive index [11]. Future work will focus on smoothing the surface to reduce the scattering loss.

![Graph showing waveguide modes and porosity](image)

**Fig. 2.** Measured (solid lines) and calculated (dashed lines) attenuated total reflectance spectra of two different polymer-cladded PSi waveguides. The resonance at lower angle corresponds to a first order mode supported by the 56% porosity PSi waveguide and the higher angle resonance corresponds to a zeroth order mode supported by the 65% porosity PSi waveguide.

### 3. SENSITIVITY AND QUALITY FACTOR CALCULATIONS

#### 3.1 Sensitivity comparison using first order perturbation theory

Given the experimental results demonstrating the feasibility of fabricating and characterizing polymer-cladded PSi waveguides, we explore the theoretical capabilities of the multilayer waveguide structure for sensing applications. Both polymer and gold cladding layers are considered. First order perturbation theory is used to determine the sensitivity of the waveguides to small changes in refractive index caused by the attachment of molecules in the PSi layer. The refractive index change $\Delta n$, or change in dielectric constant $\Delta \varepsilon$, causes a corresponding change of the effective index of the guided wave. First order perturbation theory is a proper method to analyze mode index changes due to small molecule attachment as long as the total index change is small compared to the original index value. Under these conditions, the change of effective index of the guided wave is calculated by Eq. (1) for TE waves [12, 13].

$$
\Delta N = \frac{\int_{-\infty}^{\infty} \Delta \varepsilon(z) \left[ E(z) \right]^2 dz}{\int_{-\infty}^{\infty} \left[ E(z) \right]^2 dz}
$$

(1)
The electric field in each layer of the waveguide structure can be found based on transfer matrix theory [14], and the thickness of the cladding layer is optimized based on the pole expansion method described in [15, 16]. Rewriting \( \Delta \varepsilon(z) = 2n \cdot \Delta n \) and \( \Delta \left( N^2 \right) = 2N \cdot \Delta N \) in Eq. (1), we find
\[
\frac{\Delta N}{\Delta n} = \frac{n_1}{N} \frac{P_{\text{PSi}}}{P_{\text{total}}}
\]
where the ratio \( P_{\text{PSi}}/P_{\text{total}} \) is the power confinement factor, defined as
\[
P_{\text{PSi}} = \frac{\int_{-\infty}^{\infty} \left[ E(z) \right]^2 \, dz}{\int_{-\infty}^{\infty} \left[ E(z) \right]^2 \, dz}.
\]
The power confinement factor is the ratio of the power confined in the PSi layer to the total power distributed throughout the entire waveguide region. The sensitivity of the PSi waveguide sensor, in the case of angular interrogation, is defined as given in Eq. (4).
\[
\text{sensitivity} = \frac{d \theta}{dn} = \frac{d \theta}{dN} \cdot \frac{dN}{dn}
\]
Since we can define \( N = n_1 \sin \theta \), based on the requirement that the tangential component of the incident wave vector in the prism matches the wave number of a guided mode, we find the following analytical expression of the sensitivity of the waveguide:
\[
\text{sensitivity} = \frac{P_{\text{PSi}}}{P_{\text{total}}} \cdot \frac{n_1}{N} \cdot \frac{1}{n_1 \cos \theta}.
\]
From Eq. (5), it is clear that the sensitivity is proportional to the power confinement factor and incident angle, and inversely proportional to the effective index.

In order to understand the relative contributions of the power confinement factor and incident angle on device sensitivity, Fig. 3 (a-c) shows the calculated resonance angle, power confinement factor, and sensitivity of polymer and gold-cladded PSi waveguides, respectively, as a function of the porosity of a 1 \( \mu \)m thick PSi waveguide layer, assuming a wavelength of 1550 nm. The corresponding optical thicknesses of the PSi films are also provided for reference. The dielectric constants of the polymer and gold films at 1550 nm are 2.25 and -114.925-11.0918j, respectively [17].
It can be seen from Fig. 3 (a) that polymer-cladded PSi waveguides always require a larger incident angle to excite a guided mode for a given PSi membrane porosity compared to gold-cladded waveguides due to the higher effective indices of polymer-cladded PSi waveguide modes. The difference in resonance angle becomes larger with the increase of the order of the mode since the effective indices of higher order modes are more strongly influenced by the cladding refractive index. For example, the 3rd order mode the polymer-cladded waveguide requires an incident angle in the prism that is ~10° larger than required by a gold-cladded waveguide; the resonance angle difference for 0th order modes is only ~1°. Fig. 3 (b) shows that gold-cladded waveguides have superior power confinement than polymer-cladded waveguides due to the higher refractive index contrast between the PSi and cladding layers. As observed from Fig. 3 (c), larger confinement factors do not necessarily lead to more sensitive biosensors. All of the contributing factors in Eq. (5) must be taken into account. The calculated sensitivities for both polymer- and gold-cladded waveguides with respect to the porosity of the 1 μm thick PSi waveguide layer are shown in Fig. 3 (c). Sensitivities in excess of 200 degrees/RIU are achievable for optimized structures. For each mode, the sensitivity decreases with increasing porosity until a cutoff porosity for the mode is satisfied. The cutoff porosity corresponds to the wave vector condition $k_a = k_{a1}$, in the PSi layer. For very large incident angles, the sensitivity of each mode increases rapidly due to the dependence of $\theta$ in Eq. (5). The second cutoff porosity for each mode therefore corresponds to $\theta$=90°. Based on Fig. 3, we conclude that there is no obvious advantage of using gold or polymer as the cladding material when considering the sensitivity of the waveguide sensor. We note for comparison, the sensitivity of traditional SPR sensors at 633 nm (1550 nm) to small molecule attachment is ~0.57 degree/RIU (0.15 degree/RIU).
3.2 Quality factor comparison

Evaluation of the overall sensor performance is not limited to sensitivity. The accuracy of detecting resonance shifts due to molecular binding must also be considered. It is more challenging to accurately quantify small angular deviations of broad resonance dips compared to narrow resonances with steep slopes. Furthermore, the sensor response time should be considered as it is preferable to detect binding events as rapidly as possible. Therefore, we introduce a quality factor in Eq. (6) to compare the overall performance of optical biosensors.

\[
\text{Quality factor} = \frac{\text{sensitivity}}{\text{FWHM} \cdot \text{thickness}}
\]  

(6)

The quality factor takes into account the sensitivity of the sensor, full-width-at-half-maximum (FWHM) of the resonance, and thickness of the active sensor region where molecules interact with the electric field. We note that the units of quality factor are given as \((\text{RIU} \cdot \mu\text{m})^{-1}\). From Eq. (6), it is evident that a smaller FWHM and larger detection sensitivity are desired because a narrower resonance feature allows more efficient detection of the resonance shift and precise analysis of the sensitivity. In addition, thinner active sensor regions promote faster sensor response.

The FWHM of polymer and gold-cladded PSi waveguides is determined based on the resonance angle and total loss of the entire structure [16]. With the optimized cladding layer thickness, the FWHM of the resonance dip can be expressed by

\[
\text{FWHM} = \frac{4\gamma}{(2\pi/\lambda)n_p \cos \theta}
\]  

(7)

where \(\gamma\) is the imaginary part of the wave vector, which describes the total loss of the entire structure and \(n_p\) is the refractive index of the prism.

While it is clear from Eq. (5) that sensitivity is independent of the loss of the multilayer waveguide structure, the FWHM of the resonance dip is highly dependent on losses. If the total losses go to zero, the FWHM of the resonance dip also goes to zero, and no resonance feature is observed in the ATR spectrum. For polymer-cladded PSi waveguides, the only source of total loss is from absorption and scattering losses in the PSi layer because the polymer layer is assumed to be lossless (<0.5dB/cm). For gold-cladded waveguides, an additional loss mechanism introduced by the gold layer contributes to the total loss of the multilayer waveguide due to the large absorption loss of gold. In many cases, the gold absorption loss is the dominant loss of the entire structure.

In our evaluation of the quality factor, we include different effective PSI absorption losses, which take into account both material absorption and scattering losses, by directly adding different imaginary contributions to the complex refractive index of silicon \(n_{j\kappa}\). The absorption loss coefficient \(\alpha'\) (dB/cm) can be described by

\[
\alpha' = \frac{10\gamma}{\ln(10)}
\]  

(8)

with \(\gamma = (4\pi/\lambda)\kappa\). The FWHM, and therefore quality factor, change in accordance to the magnitude of different loss contributions. Fig. 4 shows the quality factors of polymer and gold-cladded PSi waveguides as a function of the imaginary part of the silicon index. As expected, the quality factor decreases as the loss contribution increases. Although a particular order of guided mode is supported over a range of PSI waveguide porosities, in Fig. 4, we choose one representative porosity for each mode (i.e., we choose porosities of 10\%, 40\%, 60\% and 70\% for 3\(^{rd}\), 2\(^{nd}\), 1\(^{st}\), and 0\(^{th}\) order modes, respectively) at which the modes have approximately the same sensitivity. For a given PSI loss value, gold-cladded PSI waveguides have significantly lower quality factors compared to those of polymer-cladded PSI waveguides due to the large absorption loss from the gold film. For low-loss PSI waveguides approaching 1 dB/cm, the quality factor exceeds 10,000. The scaling of quality factor with effective PSI absorption losses is slightly different for the polymer and gold-cladded PSI waveguides because the gold-cladded PSI waveguides have an additional gold cladding thickness dependent absorption loss that contributes to quality factor calculation. The optimized gold cladding thickness changes with the optical thickness of the PSI layer and mode order supported by the PSI waveguide.

For comparison of the performance of polymer and gold-cladded PSI waveguide sensors to traditional SPR sensors for small molecule detection, we additionally calculate the quality factor of SPR sensors based on first order perturbation theory [12, 13]. In Fig. 4 (b), the dashed line (quality factor ~ 100) and the dotted line (quality factor ~ 50) indicate the approximate quality factors of SPR sensors used to detect the attachment of thin molecular layers (<1-10nm) at wavelengths of 1550nm and 633nm, respectively. It is clear from comparing Fig. 4 (a) and (b) that for effective PSI absorption losses below 1000 dB/cm, both gold and polymer-cladded PSI waveguides have superior performance for small molecule detection compared to SPR sensors. Furthermore,
we find that polymer-cladded PSi waveguides show the best performance for all conditions considered in this theoretical analysis.

![Graph showing quality factors of polymer-cladded waveguides (a) and gold-cladded waveguides (b) as a function of the imaginary part of the silicon index. The quality factor of SPR sensors at 1550 nm (dashed line) and 633 nm (dotted line) is shown in (b). Polymer-cladded PSi waveguides exhibit significantly higher quality factors than gold-cladded waveguides and conventional SPR sensors. The inset of (a) shows that very large quality factors can be achieved for low-loss PSi waveguides.](image)

4. EXPERIMENTAL ANALYSIS OF POLYMER-CLADDED POROUS SILICON WAVEGUIDE SENSITIVITY

In order to confirm the predicted capabilities of the PSi membrane waveguides in the Kretschmann configuration, an experiment was conducted in which a thin monolayer of molecules was added to a polymer-cladded PSi waveguide. Slight modification of the fabrication protocol described in section 2.2 was necessary to allow robust attachment of molecules in the porous silicon. After forming the PSi layer at 40 mA/cm² for 35 seconds and removing the PSi film from the silicon substate, the PSi membrane was oxidized at 500°C for 5 minutes in an oven [9]. After oxidation, we estimate based on [19] that the effective refractive index of the PSi film is 1.94, which corresponds to an optical thickness of 1.9, and there is a 1.6 nm thick oxide layer on the pore walls. The oxidized PSi membrane was then attached to the polymer cladding and prism as described previously. A monolayer of 3-aminopropytriethoxysilane (APTES) was attached inside the PSi layer by dropping a solution of 4% APTES onto the PSi surface, incubating the sample in a humid environment for 20 minutes, rinsing the sample with DI water, drying the sample with nitrogen gas, and finally baking the sample at 100°C for 10 minutes.

Figure 5 shows the ATR spectra of the polymer-cladded PSi waveguide before and after molecular infiltration of APTES. A resonance shift of 0.79° is observed due to the infiltrated molecules. Based on ellipsometry measurements performed on a silicon wafer coated with a monolayer of APTES, the thickness of a monolayer of APTES on the PSi pore walls is estimated to be 0.8 nm. The refractive index of APTES at 1550 nm is taken to be approximately 1.5 [18]. Taking into consideration the oxide layer on the PSi, we find the refractive index change induced by attachment of a monolayer of silane is ~0.027 [19]. The experimental sensitivity of the polymer-cladded PSi waveguide for the detection of small molecules is therefore 29 degrees/RIU. We find a good match between this experimental sensitivity and the calculated sensitivity shown in Fig. 3 (c).
Fig. 5. Experimental ATR spectra before and after the infiltration of 3-APTES. A 0.79° resonance shift results from the index change of 0.027 after silanization, which gives a sensitivity of 29 degree/RIU for the polymer-cladded waveguide.

5. CONCLUSION

Polymer and gold-cladded porous silicon (PSi) waveguides are advantageous platforms for small molecule biosensing due to their large available surface area for molecular binding and strong field confinement in regions where molecules are bound. Theoretical calculations based on first order perturbation theory suggest that the detection sensitivities of polymer and gold-cladded PSi waveguides are in the same range while the polymer-cladded PSi waveguide show a distinct advantage in quality factor due to absorption losses in the gold cladding that lead to broader resonances. Under optimized conditions, both polymer and gold-cladded PSi waveguides have higher quality factors compared to traditional SPR sensors for small molecule detection. Experiments confirmed the predicted detection sensitivity of polymer-cladded PSi waveguides although future work is necessary to minimize scattering losses from the PSi film and reduce the FWHM of the resonance.

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