Porous Silicon Waveguide with Integrated Grating Coupler for DNA Sensing

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ABSTRACT

A porous silicon waveguide with integrated grating coupler is demonstrated as a new platform for portable detection of chemical and biological molecules. The two-layer porous silicon waveguide is formed by electrochemical etching and a photore sist grating is fabricated directly on the waveguide core by means of electron beam lithography. Angle-resolved reflectance measurements reveal distinct peaks corresponding to the guided mode. A 0.420° reflectance shift was observed upon 16-base DNA hybridization, which was more than a factor of 5 larger than the observed reflectance shift after exposure to a mismatched DNA sequence.

Keywords: Porous silicon, DNA, Waveguide, Grating

1. INTRODUCTION

Porous silicon is a crystalline form of the element silicon that has void spaces introduced into its microstructure. In this work, we focus on porous silicon with nanoscale void spaces, although the void spaces in porous silicon films can be as large as several microns. With void spaces much smaller than the wavelength of light, porous silicon films are treated as effective media; the refractive indices of these films are directly related to their porosity. Consequently, many thin film multilayer structures, such as Bragg mirrors, rugate filters, and microcavities, can be fabricated out of porous silicon. For our present work, we discuss the fabrication, characterization, and future applications of two layer porous silicon waveguides. Porous silicon waveguide initially appeared as bridges to interconnect optoelectronic components in the early 1990’s. The straightforward electrochemical fabrication process, which is compatible with traditional silicon manufacturing techniques, enables the potential integration of porous silicon components with electronic components on-chip [1-3]. In the late 1990’s, porous silicon waveguide were first studied for sensing applications. H. F. Arrand used a porous silicon waveguide as a solvent detector based on its degrees of loss reduction when filled with different liquids [4, 5]. Gas sensing was also performed using porous silicon waveguides based on absorption [6] and optical scattering measurements [7]. Recently, very high sensitivity porous silicon waveguides for small molecule detection were proposed [8] and demonstrated [9-11] by means of attenuated total reflectance measurements.

In this work, a porous silicon waveguide with grating coupler is introduced as an advanced component for integrated optical chip biosensors. Compared to the previously reported prism-coupled porous silicon waveguides relying on attenuated total reflectance measurements, the grating-coupled waveguide has similar sensitivity but more a more compact design with greater potential for integration with microfluidics and usage outside of a clinical setting.

In section 2, the design, fabrication procedure, and method of characterization of porous silicon waveguides with lithographically defined photore sist grating couplers are provided. In section 3, we discuss the application of the grating-
couple porous silicon waveguide for DNA sensing. The attachment of chemical cross-linkers and probe DNA oligos is verified, and the performance of the porous silicon waveguide sensors for the identification of 16-base DNA sequences is demonstrated.

2. POROUS SILICON WAVEGUIDE WITH GRATING COUPLER

2.1 Porous silicon waveguide with grating coupler

Figure 1 shows a scanning electron microscopy (SEM) image of a typical porous silicon waveguide with a 340 nm upper porous silicon layer of 61% porosity (refractive index of 1.81 at a wavelength of 1550 nm) and a 1500 nm lower porous silicon layer of 84% porosity (refractive index of 1.26 at a wavelength of 1550 nm). Details regarding the porous silicon are given in section 2.2.1. The two layer porous silicon structure serves as a waveguide due to the total internal reflection of light in the top porous silicon layer, which has a higher index of refraction than the air cover above and the low refractive index porous silicon layer below. Since light is well-confined in the upper porous silicon layer, it is difficult not only to extract light from the waveguide but also to couple light into the waveguide [12]. In this work, a grating was employed to allow external light to couple into and out of the waveguide in a more compact way than using a prism to provide the same functionality. At a particular incident angle, diffracted light from the grating possess the same horizontal wavevector as a guided mode in the waveguide. At this angle, light can couple into and out of the waveguide via the grating [12]. Since the wavevector of the guided mode depends on the refractive index of the waveguide, the coupling angle changes when molecules are attached inside the porous silicon waveguide. Figure 2 shows an SEM image of a typical photoresist grating on a porous silicon waveguide. It is evident that the pores are open and unobstructed between the photoresist grating lines to allow infiltration of biomolecules inside the porous silicon waveguide. We previously reported the ability to infiltrate a monolayer of 3-aminopropyltriethoxysilane (3-APTES, ~0.8Å) into the pores between the grating lines [13].

Fig.1 Cross-section SEM image of two-layer porous silicon waveguides. The bottom, high porosity porous silicon layer is truncated in this image in order to obtain sufficient magnification to resolve the morphology of the upper, low porosity porous silicon layer.
2.2 Sample fabrication procedure

2.2.1 Preparation of porous silicon waveguide

Porous silicon waveguides were electrochemically etched on p+ (0.01Ω·cm) silicon wafers in 15% ethanoic hydrofluoric acid electrolyte. Using a Keithly 2425 sourcemeter, a first current density of 5 mA·cm$^2$ was applied for 62 seconds to form a low porosity porous silicon layer. After a 2 second regeneration period [14], a second current density of 48 mA·cm$^2$ was applied for 53 seconds to form a high porosity porous silicon layer beneath the previously etched low porosity layer. Etching proceeds primarily at the pore tips such that the first porous silicon layer is not altered during the formation of the second porous silicon layer [15]. In order to widen the pores to promote biomolecule penetration into the porous silicon matrix, 100 μl of 1.5 mmol·L$^{-1}$ KOH solution was dropped on the porous silicon waveguide for 30 minutes. The waveguide was then thermally oxidized at 500°C for 5 minutes, creating a silica-like surface on the internal pore walls to facilitate biochemical functionalization.

2.2.2 Grating fabrication

Complete grating fabrication details can be found in [13]. Briefly, a 400 nm film of ZEP 520A photoresist (Zeon Corp.) was spun onto a porous silicon waveguide and exposed by a JEOL-9300FS electron beam lithography tool to form a diffraction grating with a grating period of approximately 1590 nm. The photoresist grating was developed by a 30 second immersion in xylenes solution.

2.3 Instrumentation

A Metricon Model 2010/M Prism Coupler was used with the prism removed in the non-contact, VAMFO (variable-angle monochromatic fringe observation) mode to monitor the reflectance properties of the porous silicon waveguide sensor during functionalization and after exposure to various DNA oligos. The prism coupler has a resolution of 0.002°. A 1550 nm diode laser was used as the light source; the near-infrared region corresponds to a region of low absorption losses in silicon that does not interfere with traditional biological absorption lines.

A schematic of the measurement configuration for the grating coupled porous silicon waveguides is shown in Fig. 3. Light from the diode laser is incident on the waveguide at variable angle, and the reflected light intensity is measured by a photodetector. Figure 4 shows the measured reflectance as a function of incident angle of a porous silicon waveguide with and without a photoresist grating coupler. The resonance features are only present in the waveguide with the...
diffraction grating, further demonstrating the need for the grating coupler to enable guided wave propagation in the porous silicon. It should be noted that the resonance near 38° corresponds to a field distribution almost entirely confined in the upper porous silicon layer, while the other resonant features in the spectrum correspond to field distributions that extend significantly into the grating [13].

![Schematic of the measurement configuration for the grating coupled porous silicon waveguides.](image)

**Fig. 3** Schematic of the measurement configuration for the grating coupled porous silicon waveguides.

![Angle-resolved reflectance spectra of porous silicon waveguide with (solid line) and without (dotted line) the grating coupler. Resonant features are only present in the grating coupled waveguide.](image)

**Fig. 4** Angle-resolved reflectance spectra of porous silicon waveguide with (solid line) and without (dotted line) the grating coupler. Resonant features are only present in the grating coupled waveguide.

### 3. DNA SENSING WITH GRATING COUPLED POROUS SILICON WAVEGUIDE

#### 3.1 Functionalization

In order to attach probe DNA oligos to oxidized porous silicon waveguides, an organofunctional silane, 3-aminopropyltriethoxysilane (3-APTES), which has a terminal amine group, was used to modify the silica surface. The oxidized porous silicon waveguide samples were soaked in the 4% 3-APTES solution for 20 minutes. Then they were rinsed with deionized water and baked at 100°C for 10 minutes.

Next, the silanized porous silicon waveguides were incubated in 2.5 mg·mL⁻¹ Sulfo-L-Cystamine (Pierce) solution for 2 hours, followed by a 1 hour soaking
in HEPES buffer, rinsing with deionized water, and drying with nitrogen gas. Thiol modified probe DNA oligos were attached by dropping 100 μL of 100 μmol·L⁻¹ probe DNA (5’-TAG CTA TGG TCC TCG T-3’, 3’ Thiol C3, MWG-Biotech) on the porous silicon waveguide samples. After 1 hour incubation, the porous silicon waveguide samples were soaked in HEPES buffer for 20 minutes, rinsed with deionized water, and dried with nitrogen gas.

Reflectance measurements were taken, using the setup shown in Fig. 4, after each functionalization step in order to confirm the attachment of the silane, cross-linker, and probe DNA molecules. Figure 5 shows the reflectance spectra of a grating coupled porous silicon waveguide after the attachment of 3-APTES, Sulfo-SMCC, and probe DNA. Focusing on the resonance near 38°, it can be seen that the peak shift after Sulfo-SMCC attachment is almost two times larger than the shift due to attachment of 3-APTES, which is consistent with their molecular weights (3-APTES: 221 daltons, Sulfo-SMCC: 436 daltons). Based on the magnitudes of these shifts, it is believed that complete monolayers of 3-APTES and Sulfo-SMCC are formed on the pore walls of the waveguide. It is noted that if these chemicals were attached only on the surface of the waveguide, a significantly smaller resonance shift would result [9]. Given the size of the probe DNA oligos, the peak shift after probe DNA attachment was smaller than expected, suggesting that there is a relatively low probe density in the porous silicon waveguide. DNA immobilization may have been inhibited in part by the small pore diameters of approximately 30 nm [16].

In order to demonstrate the small molecule biosensing capabilities of our structures, two functionalized grating-coupled porous silicon waveguides were spotted separately with 100 μmol·L⁻¹ of antisense (5’-ACG AGG ACC ATA GCT A-3’, complementary strand to probe DNA) and mismatch (5’-GGT TTC TGA TGC TGA C-3’, non-complementary strand to probe DNA) DNA. After 1 hour incubation at 37°C, the waveguides were soaked in HEPES buffer for 20 minutes to rinse out the non-hybridized oligos. Figure 6(a) shows a 0.420° resonance shift after the hybridization of antisense, suggesting that the porous silicon waveguide is indeed capable of detecting DNA sequences. In demonstration of the selectivity of this detection, Fig. 6(b) shows a much smaller 0.075° resonance shift due to non-specifically bound mismatch DNA. Slight modification of the rinsing protocol, immobilization procedure, and porous silicon pore size is expected to reduce the magnitude of this non-specific shift. The magnitude of the resonance shifts after hybridization and exposure to mismatch DNA are reproducible upon measurement of multiple samples. For comparison, a third functionalized porous silicon waveguide was exposed to HEPES buffer for 1 hour at 37°C. As shown in Fig. 6(c), negligible shift results, confirming the stability of the sensor.

Fig. 5 Grating coupled porous silicon waveguide reflectance spectra after oxidation and attachment of 3-APTES, Sulfo-SMCC, and probe DNA. The resonance shifts confirm the attachment of these molecules in the oxidized porous silicon waveguide.

3.2 DNA oligo identification

In order to demonstrate the small molecule biosensing capabilities of our structures, two functionalized grating-coupled porous silicon waveguides were spotted separately with 100 μmol·L⁻¹ of antisense (5’-ACG AGG ACC ATA GCT A-3’, complementary strand to probe DNA) and mismatch (5’-GGT TTC TGA TGC TGA C-3’, non-complementary strand to probe DNA) DNA. After 1 hour incubation at 37°C, the waveguides were soaked in HEPES buffer for 20 minutes to rinse out the non-hybridized oligos. Figure 6(a) shows a 0.420° resonance shift after the hybridization of antisense, suggesting that the porous silicon waveguide is indeed capable of detecting DNA sequences. In demonstration of the selectivity of this detection, Fig. 6(b) shows a much smaller 0.075° resonance shift due to non-specifically bound mismatch DNA. Slight modification of the rinsing protocol, immobilization procedure, and porous silicon pore size is expected to reduce the magnitude of this non-specific shift. The magnitude of the resonance shifts after hybridization and exposure to mismatch DNA are reproducible upon measurement of multiple samples. For comparison, a third functionalized porous silicon waveguide was exposed to HEPES buffer for 1 hour at 37°C. As shown in Fig. 6(c), negligible shift results, confirming the stability of the sensor.

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Fig. 6 Resonance shifts of grating-coupled porous silicon waveguides after exposure to (a) antisense DNA, (b) mismatch DNA, and (c) HEPES buffer. In (b), the reflectance amplitudes before and after exposure to the mismatch DNA are slightly different due to the instrument configuration, which does not affect the resonance angle positions.

4. CONCLUSIONS

A label-free porous silicon waveguide with a grating coupler was studied for small molecule biosensing applications. The use of a grating coupler instead of a prism coupler allows the device to be more compact. The large surface area available inside the waveguide for biomolecule immobilization and capture, and the guided mode interaction with these molecules offer significant advantages for integrated optical chip sensors. Through variable angle reflectance measurements, 16-base antisense DNA oligos were clearly distinguished from mismatch DNA oligos.

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