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ABSTRACT

Porous silicon waveguiding is a promising platform for biosensing and chemical sensing applications. In this work, we review current progress in the emerging field of porous silicon waveguides and discuss various sensing techniques involving the guided mode waveguiding platform. General setups include waveguide interferometric setups, high confinement interferometry, grating coupler guided mode waveguides, photonic crystal resonators and ring resonator porous silicon waveguides. The porous silicon waveguide platform sets up the biosensing platform for an ultra-high sensitivity for biological and chemical sensing applications.

Introduction

Biomolecule detection is crucial to various field applications such as medical diagnostics, detecting pollutants and carcinogens and food safety. Optical sensing is a rising platform for waveguide based on chip biosensing that are capable of label-free biosensing where sensing can be performed without any labels or fluorophores[1–3]. This gets rid of extra biomolecules that can harm the chemical binding process. These label free sensors generally detect the change in refractive index, and specificity is achieved by chemical affinity binding. Analytes bound on the surface of the biosensor such as a silicon SOI waveguide[4], surface plasmon resonance[5], fiber optic waveguide[6] or photonic crystal[7], or a planar waveguide[8,9] interact with the electromagnetic waves creating a perturbation which is sensed by the assay – which is the optical sensing technique. However, the analytes only perturb the evanescent field which does not result in optimal performance because the interaction between analyte and the guided mode is not optimal. To optimize the overlap, porous materials have been proposed due to their high surface area which results in high surface coverage.

Porous silicon is an attractive material because if its large surface area[10–12]. Biomolecules can seep into the pores making it a prime candidate for molecular sensing[13]. Numerous breakthrough techniques have been demonstrated using porous silicon waveguides[8,12,14–16]. Some of them include high confinement waveguides[15], ring resonators[10–12], strip waveguides[8], grating coupled waveguides[17], photonic crystal resonators[18] and so on. Other notable works include porous silicon rugate filters[19,20], thin film interferometers[21], resonant microcavities[22] etc.

Fabrication

Porous silicon is fabricated in a repeatable chemical process that allows tunable porosity, pore size and thin film thickness[23]. The porosity can be axially changed which allows for a refractive

index gradient from top to bottom[24]. The fabrication process does not allow a lateral refractive index variation. However, this can be achieved by a recently demonstrated technique which is an imprinting technique[25,26]. But this does not help in biosensing as the imprinted porous silicon has tiny closed pores. Porous silicon is generally fabricated by electrochemically etching silicon wafers or dies in an aqueous or ethanoic HF solution. The porosity is determined by the current density, HF concentration and the thickness of the etched layer is determined by the etch time. However, current density also controls the etch rate, so this must be taken into consideration.

Generally porous silicon wafers are diced in to dies and then anodized in ethanoic HF. Multilayer waveguides with current densities of 4.92 mA/cm2 and 55 mA/cm2 result in a refractive index of 2.1 and 1.56 RIU which act as the core and cladding layers respectively. This can be arbitrarily etched to create multilayer waveguides of any dimensions. The lateral waveguide dimension can be determined by well-established lithographic techniques such as photolithography, or electron beam lithography. Axial dimensions of the waveguide layers can be modified using varying etch times. The wafers can be turned into pSi first, and then lithography can be performed. Or lithography can be performed first, and then the structure would be turned into pSi. In this case, the waveguide would take on an interesting shape, as observed in this work[15]. However, grating coupled waveguides are also fabricated and used for biosensing. This is done by either considered photoresist printed grating or lithographically etched grating[17]. Silicon on insulator grating coupler sensors also exist, but they demonstrate a much lower analyte-sensor overlap, resulting in a lower sensitivity. This is demonstrated by Wei et al where they compare resonance angle shifts for PSi grating, resist grating and SOI grating coupled waveguides. The PSi sensor comes out on top and outperforms the other two. This is because fundamentally the SOI operates by the perturbations caused by analytes sticking outside the waveguide walls. On the contrary,

PSi waveguide sensors see further perturbations caused by molecules stuck in the pore walls inside the waveguides.

Surface Chemistry and Characterization

Research demonstrations regarding PSi biosensors include protein sensing[27], DNA sensing[28] and PNA sensing. Surface sensitivity is generally characterized by silane functionalization[29]. Several biomolecule detections can be carried out on top of the silane functionalized layer that includes the protein and DNA sensing[30]. However, we must note that DNA functionalization has corrosion effects[31]. Protein sensing comprises of Biotin-Avidin sensing[32]. DNA sensing generally starts with 3-APTES and then there can be an intermediate step with Sulfo-SMCC, Glutaraldehyde or SPDP[30]. The probe DNA is then attached which can be used to hybridize complementary DNA strands.

Sensor characterization is generally performed with oxidation of the porous silicon to functionalize it for 3-APTES attachment. Oxidation at 500 C for 5-10 minutes is sufficient to create a thin oxide layer for silane attachment[33]. Up to 4% 3-APTES can be used and there can be several combinations. 3-APTES can be diluted in anhydrous toluene, methanol, or ethanol. Even though 3-APTES can be diluted in DI water, hydrolysis can occur. However, some literature suggests hydrolysis can be avoided by leaving 3-APTES diluted in the shelf for long term storage. 3-APTES can also be used with a mixture of 1:1 DI water and methanol/ethanol. For 4% 3-APTES, incubation time of about 25 minutes can be recommended for a silane monolayer, which has a nominal layer thickness of 0.8 nm which generally results in a ~32 nm wavelength shift in a ~75% porosity silicon thin film[29].

For protein sensing, biotin attachment can be carried out using EzLink Sulfo-NHS-Biotin, Sulfo-NHS-LC Biotin or NHS-PEG-Biotin. Biotin can be attached on the 3-APTES surface by diluting it in DI Water. Biotin reagents are available from Thermo Fisher or Sigma Aldrich that are soluble in water. Generally, 5mg/ ml or 2.5 mg/ml concentration can be used. Some may consider this rather high, but a high concentration probe can be used to detect a low concentration protein (Avidin or Streptavidin).

DNA sensing can be non-trivial. On 3-APTES functionalized porous silicon surface, we can use Sulfo-SMCC or Glutaraldehyde[14] as a homo-bifunctional or a hetero-bifunctional cross linker. Probe DNA then can be attached to it and then hybridization experiments can be performed. We'd like to say that because of the inherent positive charge of the DNA, the porous silicon skeletons are prone to corrosion if there is no sufficient surface passivation[28].

Sensor Performance

Porous silicon waveguide biosensing simply outperform existing waveguide sensing techniques such as the SOI due to higher modal overlap with the analyte. Near 100% overlap is shown by some recent demonstrations that can detect the bulk refractive index change and, in some cases, even more due to waveguide dispersion effects. However, even traditional porous silicon waveguides get over 40% modal overlap even without any waveguide engineering, making it much more sensitive. However, performance metrics must be quantized so the porous silicon waveguide biosensor can be compared quantifiably to state of the art biosensing techniques like the Surface Plasmon Resonance (SPR). Some unrelated metrics to performance are easy of use, scalability, easy of fabrication and characterization.

Quantitative sensor performance can be characterized by several parameters: 1. Sensitivity, 2. Detection time, 3. Specificity and 4. Limit of detection.

Sensitivity is a key factor in biosensor performance and defined by the change in resonant wavelength which can be a result of the refractive index change in the bulk effective medium. The sensors that are able to detect the maximum amount of change per minimum analyte attachment are said to be more sensitive. This sensitivity can be defined in a few ways. Sensitivity can be defined by resonant wavelength change per adlayer thickness:

$$S_1 = \frac{\delta\lambda}{\delta\sigma}$$

Then again, the change in wavelength shift is due to a change in the bulk refractive index, so sensitivity can also be defined by:

$$S_2 = \frac{\delta\lambda}{\delta n}$$

The change in refractive index is due to the change in adlayer thickness so the bulk refractive index sensitivity is a characteristic of average pore size. This is given by:

$$S_3 = \frac{\delta n}{\delta\sigma}$$

Grating coupled waveguide sensors demonstrated here[34] work based on the angle change per refractive index change. Here, the detection limit is limited by the resolution of the measurement instrument that measures the angle. Wei et al demonstrate a grating coupled porous silicon waveguide that detects DNA and PNA hybridization[17]. These waveguides show a 32-fold higher field distribution where molecules can bind compared to grating-coupled SOI waveguides.

Another measurement method is directly measuring the group index in an interferometric setup. This also opens the degree of freedom for engineering the waveguide dispersion with multilayer waveguides[35]. Photonic crystal nanobeam waveguides are also demonstrated for DNA and PNA sensing[10] which shows up to 10 time as much performance boost compared to nanobeam photonic crystal SOI[36].

Conclusion

We review the advances in waveguide based porous silicon sensors and they prove to be a solid choice for on-chip sensing. They offer a lot of choices in terms of novel optical sensing techniques and the ultra-high surface area allows it to be a better sensor than most non-porous waveguide based sensors. However, further optimization is required to lower the losses to make it a scalable high performance platform in the biosensing field.

References

(1) Thevenot, D. R.; Toth, K.; Durst, R. A.; Wilson, G. S. Technical Report Electrochemical Biosensors : Recommended Definitions and Classification. **2001**, *16*, 121–131.

(2) Perez, J. M.; Josephson, L.; Loughlin, T. O.; Högemann, D.; Weissleder, R. Magnetic Relaxation Switches Capable of Sensing Molecular Interactions. **2002**, *20* (August). https://doi.org/10.1038/nbt720.

(3) Zhuo, Y.; Cunningham, B. T. Label-Free Biosensor Imaging on Photonic Crystal Surfaces. *Sensors (Switzerland)* **2015**, *15* (9), 21613–21635. https://doi.org/10.3390/s150921613.

(4) TalebiFard, S.; Schmidt, S.; Shi, W.; Wu, W.; Jaeger, N. A. F.; Kwok, E.; Ratner, D. M.; Chrostowski, L. Optimized Sensitivity of Silicon-on-Insulator (SOI) Strip Waveguide Resonator Sensor. *Biomed. Opt. Express* **2017**, *8* (2), 500. https://doi.org/10.1364/BOE.8.000500.

(5) Nguyen, H. H.; Park, J.; Kang, S.; Kim, M. Surface Plasmon Resonance: A Versatile Technique for Biosensor Applications. **2015**, 10481–10510. https://doi.org/10.3390/s150510481.

(6) Leung, A.; Shankar, P. M.; Mutharasan, R. A Review of Fiber-Optic Biosensors. **2007**, *125*, 688–703. https://doi.org/10.1016/j.snb.2007.03.010.

(7) Zhuo, Y.; Hu, H.; Chen, W.; Lu, M.; Tian, L.; Yu, H.; Long, K. D.; Chow, E.; King, W. P.; Singamaneni, S.; Cunningham, B. T. Single Nanoparticle Detection Using Photonic Crystal Enhanced Microscopy. *Analyst* **2014**, *139* (5), 1007–1015. https://doi.org/10.1039/C3AN02295A.

(8) Loni, A.; Canham, L. T.; Berger, M. G.; Arens-Fischer, R.; Munder, H.; Luth, H.; Arrand, H. F.; Benson, T. M. Porous Silicon Multilayer Optical Waveguides. *Thin Solid Films* **1996**, *276* (1), 143–146. https://doi.org/https://doi.org/10.1016/0040-6090(95)08075-9.

(9) Testa, G.; Persichetti, G.; Bernini, R. Liquid Core ARROW Waveguides: A Promising Photonic Structure for Integrated Optofluidic Microsensors. *Micromachines* **2016**, *7* (3). https://doi.org/10.3390/mi7030047.

(10) Rodriguez, G. A.; Hu, S.; Weiss, S. M. Porous Silicon Ring Resonator for Compact, High Sensitivity Biosensing Applications. *Opt. Express* **2015**, *23* (6), 7111.

https://doi.org/10.1364/OE.23.007111.

(11) Caroselli, R.; Ponce-Alcántara, S.; Quilez, F. P.; Sánchez, D. M.; Morán, L. T.; Barres, A. G.; Bellieres, L.; Bandarenka, H.; Girel, K.; Bondarenko, V.; García-Rupérez, J. Experimental Study of the Sensitivity of a Porous Silicon Ring Resonator Sensor Using Continuous In-Flow Measurements. *Opt. Express* **2017**, *25* (25), 31651–31659. https://doi.org/10.1364/OE.25.031651.

(12) Azuelos, P.; Girault, P.; Lorrain, N.; Dumeige, Y. Optimization of Porous Silicon Waveguide Design for Micro-Ring Resonator Sensing Applications. *J. Opt.* **2018**, *20* (085301), 1–13.

(13) Mariani, S.; Robbiano, V.; Strambini, L. M.; Debrassi, A.; Egri, G.; Dähne, L.; Barillaro, G. Layer-by-Layer Biofunctionalization of Nanostructured Porous Silicon for High-Sensitivity and High-Selectivity Label-Free Affinity Biosensing. *Nat. Commun.* **2018**, *9* (1). https://doi.org/10.1038/s41467-018-07723-8.

(14) Rong, G.; Ryckman, J. D.; Mernaugh, R. L.; Weiss, S. M. Label-Free Porous Silicon Membrane Waveguide for DNA Sensing. *Appl. Phys. Lett.* **2008**, *93* (16), 161109. https://doi.org/10.1063/1.3005620.

(15) Tahmid H. Talukdar, Gabriel D. Allen, Ivan Kravchenko, and Judson D. Ryckman. Single-Mode Porous Silicon Waveguide Interferometers with Unity Confinement Factors for Ultra-Sensitive Surface Adlayer Sensing. **2019**, *27* (16), 22485–22498.

(16) Mangaiyarkarasi, D.; Sheng, O. Y.; Breese, M. B. H.; Fuh, V. L. S.; Xioasong, E. T. Fabrication of Large-Area Patterned Porous Silicon Distributed Bragg Reflectors. *Opt.*

Express **2008**, *16* (17), 12757–12763. https://doi.org/10.1364/OE.16.012757.

(17) Wei, X.; Weiss, S. M. Guided Mode Biosensor Based on Grating Coupled Porous Silicon Waveguide. *Opt. Express* **2011**, *19* (12), 11330–11339. https://doi.org/10.1364/OE.19.011330.

(18) Rodriguez, G. A.; Markov, P.; Cartwright, A. P.; Choudhury, M. H.; Afzal, F. O.; Cao, T.; Halimi, S. I.; Retterer, S. T.; Kravchenko, I. I.; Weiss, S. M. Photonic Crystal Nanobeam Biosensors Based on Porous Silicon. *Opt. Express* **2019**, *27* (7), 9536. https://doi.org/10.1364/oe.27.009536.

(19) Lorenzo, E.; Oton, C. J.; Capuj, N. E.; Ghulinyan, M.; Navarro-Urrios, D.; Gaburro, Z.; Pavesi, L. Porous Silicon-Based Rugate Filters. *Appl. Opt.* **2005**, *44* (26), 5415–5421. https://doi.org/10.1364/AO.44.005415.

(20) Ishikura, N.; Fujii, M.; Nishida, K.; Hayashi, S.; Diener, J. Dichroic Rugate Filters Based on Birefringent Porous Silicon Abstract : *Opt. Express* **2008**, *16* (20), 5091–5094.

(21) Lin, V. S. Y.; Motesharei, K.; Dancil, K. P. S.; Sailor, M. J.; Ghadiri, M. R. A Porous Silicon-Based Optical Interferometric Biosensor. *Science (80-.).* **1997**, *278* (5339), 840–843. https://doi.org/10.1126/science.278.5339.840.

(22) Yoshie, T.; Tang, L.; Su, S. Y. Optical Microcavity: Sensing down to Single Molecules and Atoms. *Sensors* **2011**, *11* (2), 1972. https://doi.org/10.3390/s110201972.

(23) Jane, A.; Dronov, R.; Hodges, A.; Voelcker, N. H. Porous Silicon Biosensors on the Advance. *Trends Biotechnol.* **2009**, *27* (4), 230–239. https://doi.org/10.1016/j.tibtech.2008.12.004.

(24) Krueger, N. A.; Holsteen, A. L.; Kang, S. K.; Ocier, C. R.; Zhou, W.; Mensing, G.; Rogers, J. A.; Brongersma, M. L.; Braun, P. V. Porous Silicon Gradient Refractive Index Micro-Optics. *Nano Lett.* **2016**, *16* (12), 7402–7407. https://doi.org/10.1021/acs.nanolett.6b02939.

(25) Ryckman, J. D.; Liscidini, M.; Sipe, J. E.; Weiss, S. M. Direct Imprinting of Porous Substrates: A Rapid and Low-Cost Approach for Patterning Porous Nanomaterials. *Nano Lett.* **2011**, *11* (5). https://doi.org/10.1021/nl1028073.

(26) Talukdar, T. H.; Perez, J. C.; Ryckman, J. D. Nanoimprinting of Refractive Index: Patterning Subwavelength Effective Media for Flat Optics. *ACS Appl. Nano Mater.* **2020**. https://doi.org/10.1021/acsanm.0c01395.

(27) Mariani, S.; Pino, L.; Strambini, L. M.; Tedeschi, L.; Barillaro, G. 10 000-Fold Improvement in Protein Detection Using Nanostructured Porous Silicon Interferometric Aptasensors. *ACS Sensors* **2016**, *1* (12), 1471–1479. https://doi.org/10.1021/acssensors.6b00634.

(28) Rong, G.; Najmaie, A.; Sipe, J. E.; Weiss, S. M. Nanoscale Porous Silicon Waveguide for Label-Free DNA Sensing. *Biosens. Bioelectron.* **2008**, *23* (10), 1572–1576. https://doi.org/10.1016/j.bios.2008.01.017.

(29) Talukdar, T. H. Porous Silicon Photonics at Unity Confinement Factors for Surface Adlayer Biosensing, Clemson University, 2019.

(30) Rodriguez, G. A. Advanced Porous Silicon Photonic Devices, 2016.

(31) Rodriguez, G. A.; Lawrie, J. L.; Weiss, S. M. *Nanoporous Silicon Biosensors for DNA Sensing*; Woodhead Publishing Limited, 2014.

https://doi.org/10.1533/9780857097156.2.304.

(32) Jenie, S. N. A.; Du, Z.; McInnes, S. J. P.; Ung, P.; Graham, B.; Plush, S. E.; Voelcker, N. H. Biomolecule Detection in Porous Silicon Based Microcavities via Europium Luminescence Enhancement. *J. Mater. Chem. B* **2014**, *2* (44), 7694–7703. https://doi.org/10.1039/c4tb01409j.

(33) Morita, M.; Ohmi, T.; Hasegawa, E.; Kawakami, M.; Ohwada, M. Growth of Native Oxide on a Silicon Surface. *J. Appl. Phys.* **1990**, *68* (3), 1272–1281. https://doi.org/10.1063/1.347181.

(34) Sharon M Weiss;Judson D Ryckman; Christopher Kang; Marco Liscidini; John E Sipe. Optical Sensor Comprising Diffraction Gratings with Functionalized Pores and Method of Detecting Analytes Using the Sensor. 8349617.

(35) Judson Ryckman; Gabriel Allen; William Frederick Delaney;Tahmid Talukdar. Porous Waveguide Sensors Featuring High Confinement Factors and Method for Making the Same, 2019.

(36) Yang, D. Q.; Duan, B.; Liu, X.; Wang, A. Q.; Li, X. G.; Ji, Y. F. Photonic Crystal Nanobeam Cavities for Nanoscale Optical Sensing: A Review. *Micromachines* **2020**, *11* (1). https://doi.org/10.3390/mi11010072.