

Optimization of Porous Silicon Surface Chemistry towards Biophotonic Sensors



Kristopher A. Kilian¹, Till Böcking^{1,2}, Suhrawardi Ilyas², Katharina Gaus³, Michael Gal² and J. Justin Gooding¹

¹School of Chemistry, ²School of Physics, ³Centre for Vascular Research, School of Medical Sciences, University of New South Wales, Sydney, NSW 2052, Australia

Introduction and Aim

Porous silicon (PSi) based photonic crystals have found utility in sensing applications with a variety of multi-layered structures employed including Fabry-Perot layers¹, microcavities² and rugate filters³. In a recent report³, we demonstrated narrow-linewidth rugate filters that have the potential as sensors with high sensitivity for monitoring biological interactions.

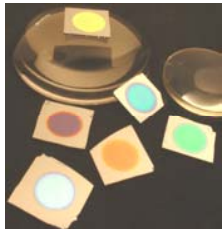


Figure 1. Porous silicon photonic crystals. The colour arises from interference of light reflected at interfaces between layers of different refractive index within the one-dimensional photonic crystal.

We have developed a protease biosensor using rugate filters modified by hydrosilylation chemistry. Incorporation of antifouling moieties and activation using standard solid-phase coupling results in a biological interface that is easily queried optically for transduction of enzyme activity.

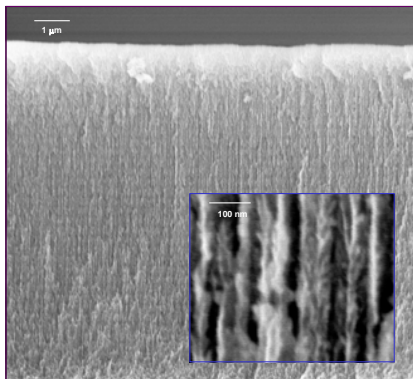


Figure 2. Scanning electron micrograph of a freshly etched 60 layer rugate filter. Inset: Close up of pore morphology demonstrating columnar pores with 30-50 nm diameter.

Method

Rugate Filter Formation

- Porous silicon rugate filters were formed as described previously³. Briefly, B-doped Si(100) wafers, resistivity 0.005 Ω cm were etched in ethanolic hydrofluoric acid (25% v/v) with a sinusoidal current density to yield structures with an average porosity between 55-65%.

Hydrosilylation, coupling and enzymatic assay

Hydride Terminated porous silicon

- PSi samples were reacted with succinimidyl undecanoate at 120° C for 16 hours.
- Reaction with hexa(ethylene oxide) amine (H₂N-EO₆) for 4 hours at room temperature
- Terminal hydroxyl activation occurred with disuccinimidyl carbonate and dimethyl amino pyridine (DMAP) for 16 hours⁴
- Incubation in angiotensin I for 6 hours at room temperature.

Scheme 1. Organic derivatization strategy for forming bioresistant multilayers and subsequent coupling of peptides as biorecognition species.

Optical Measurements

- Reflectivity spectra were measured at normal incidence using a J/Y SPEX 1681 spectrometer and silicon detector.

X-ray Photoelectron Spectroscopy

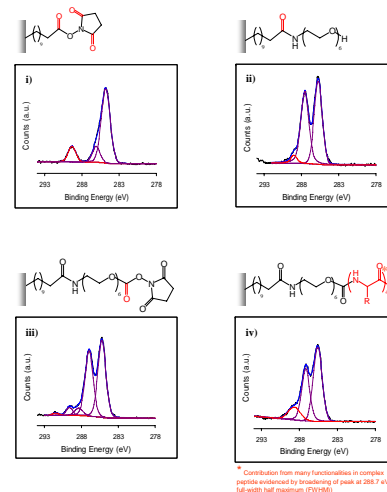


Figure 3. XP Carbon 1s spectra of porous silicon rugate filters chemically derivatized as detailed in scheme 1, i – iv. Red highlights indicate representative functional groups used to monitor reaction progression

Reflectivity

Optical reflectivity throughout organic derivatization is consistent with organic material ($n > 1.3$) replacing air ($n = 1$) in the pores.

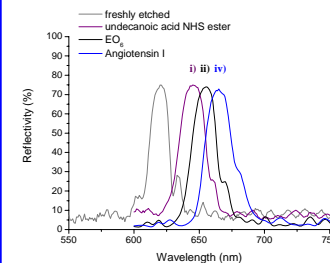


Figure 4. Optical reflectivity characterization during organic derivatization. i) a 35 nm shift, ii) a 10 nm shift and iii) to iv) a 10 nm shift. Full width half maximum maintained at 20 - 30 nm.

Monitoring Proteolytic Activity

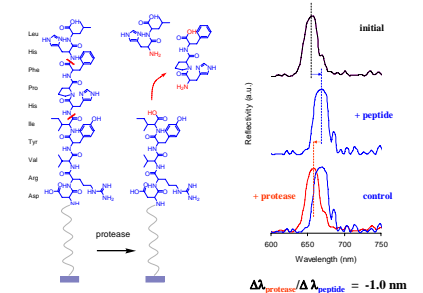


Figure 5 Left) Scheme of protease (subtilisin) action on Angiotensin I peptide with cleavage motifs adjacent to hydrophobic amino acid residues. Right) Change in reflectivity upon exposure of angiotensin I derivitized rugate filters to subtilisin.

Conclusion

Forming organic multilayers on porous silicon rugate filters effectively passivates the hydride terminated surface from oxidation whilst providing terminal coupling points for covalent attachment of biorecognition species. Exposure of protease in solution results in blue-shifting of the high reflectivity peak, consistent with enzymatic digestion of the interface. Further development is expected to lead to new classes of advanced optical devices for applications in medicine and biotechnology.

References

- Janshoff, Andreas, Dancil, Keiki-Pua S., Steinem, Claudia, Greiner, Douglas P., Lin, Victor S. Y., Gurtner, Christian, Moteschare, Kianoush, Sailor, Michael J., Ghadiri, M. Reza, *J. Am. Chem. Soc.*, 1998, 120(46), 12108
- Ouyang, Huimin, Christophersen, Marc, Viard, Romain, Miller, Benjamin L., Fauchet, Philippe M., *Adv. Funct. Mat.*, 2005, 15(11), 1851
- S. Ilyas, T. Böcking, K. Kilian, P.J. Reece, J. Gooding, K. Gaus, M. Gal, *Opt. Mater.*, 2006, In press
- T. Böcking, K. A. Kilian, T. Hanley, S. Ilyas, K. Gaus, M. Gal, and J. J. Gooding, *Langmuir*, 2005, 21, 10522

Acknowledgements

We would like to thank the Australian Research Council for funding.