Additive Combination of Spectra Reflected from Porous Silicon and Carbon/Porous Silicon Rugate Filters to Improve Vapor Selectivity

Joshua D. Kittle,* John S. Gofus III, Andrea N. Abel, and Benjamin D. Evans

ABSTRACT: Selectivity remains a challenge for rapid optical vapor sensing via light reflected from porous silicon photonic crystals. This work highlights a method to increase optical vapor selectivity of porous silicon rugate filters by analyzing additive spectra from two rugate filter substrates with different functionalities, an oxidized and carbonized surface. Individually, both porous silicon rugate filters demonstrated sensitivity but not selectivity toward the vapor analytes. However, differences in peak shift trends between the two substrates suggested differences in vapor affinities for the surfaces. By adding the two spectra, improvements to selectivity relative to the individual surfaces were observed even at low vapor pressures and for analytes of similar polarity, refractive index, and concentration. These results are expected to contribute toward optical vapor selectivity improvements in one-dimensional porous silicon photonic crystals.

INTRODUCTION

Optical vapor sensing via porous silicon photonic crystals (PhCs) remains an active area of research. Generally, PhCs are composed of a periodic structure with two or more materials with different dielectric constants. Visible light incident on a PhC with nanoscale periodicity is reflected and refracted at these periodic interfaces, giving rise to photonic band gaps (e.g., structural color). Vapor detection at low concentrations is based on changes in refractive index of the PhC brought about by microcapillary condensation of the analyte into the nanoarchitecture of the PhC. Optical vapor sensing via PhCs is of considerable interest to the environmental monitoring community due to its potential as a low-cost, continuous passive optical vapor sensor.

While a number of studies have investigated vapor sensing via both natural and synthetic PhCs, one-dimensional (1D) porous silicon (pSi) rugate filters offer a number of advantages. Both pSi rugate filters and distributed Bragg stacks (DBSs) are similar in that both use variations in pore size to change the refractive index between layers. Rugate filters, though, are formed by continuously modulating current when etching, resulting in a smooth transition in pore sizes, and thus refractive index layers, not found in DBRs. This leads to sharper photonic band gaps and absences of higher-order harmonics relative to DBRs. High-surface-area 1D PhCs from silicon are generally inexpensive to manufacture and can be tailored to various pore sizes and morphologies to increase sensitivity and selectivity. These PhCs can then be functionalized via a variety of methods to increase specificity toward analytes of interest. Porous silicon PhCs offer the additional advantage of relatively straightforward integration into microelectronics, as well as opportunities for multiparameter sensing via conductivity. Despite these advantages, significant challenges remain in using a porous silicon PhC as a sensitive, selective, rugged, passive, and inexpensive to manufacture as well as being able to be tailored to various pore sizes and morphologies to increase sensitivity and selectivity. These PhCs can then be functionalized via a variety of methods to increase specificity toward analytes of interest. Porous silicon PhCs offer the additional advantage of relatively straightforward integration into microelectronics, as well as opportunities for multiparameter sensing via conductivity.

Despite these advantages, significant challenges remain in using a porous silicon PhC as a sensitive, selective, rugged, passive, and inexpensive to manufacture as well as being able to be tailored to various pore sizes and morphologies to increase sensitivity and selectivity. These PhCs can then be functionalized via a variety of methods to increase specificity toward analytes of interest. Porous silicon PhCs offer the additional advantage of relatively straightforward integration into microelectronics, as well as opportunities for multiparameter sensing via conductivity. Despite these advantages, significant challenges remain in using a porous silicon PhC as a sensitive, selective, rugged, passive, and inexpensive to manufacture as well as being able to be tailored to various pore sizes and morphologies to increase sensitivity and selectivity. These PhCs can then be functionalized via a variety of methods to increase specificity toward analytes of interest. Porous silicon PhCs offer the additional advantage of relatively straightforward integration into microelectronics, as well as opportunities for multiparameter sensing via conductivity.

Though improvements in sensor recovery, long-term stability, and sensitivity are required, this work focuses on improving selectivity of 1D porous silicon PhCs. Some natural PhCs, such as those in wing scales of the Morpho butterfly, have a polarity gradient within their nanoarchitecture. Analytes migrate to certain regions of these natural PhCs based on their polarity, causing unique spectra shifts. However, the spectral response for a 1D porous silicon PhC depends primarily on the refractive index (n) of an analyte and its concentration, often modeled as a thin film with thickness (d). Thus, these silicon PhCs are not selective because many combinations of n and d will yield the same optical response to different vapors. To address this, a number of studies have improved the selectivity of 1D silicon-based PhCs, typically through surface functionalization or coatings, chemical reaction to alter periodic spacing, complex nanostructures, time-resolved spectroscopy, or a combination of these techniques.

Several studies have examined the spectral response of vapor analytes to pSi rugate filters with different surface functionalities.
or coatings as a means to improve selectivity. An array-based approach in which a number of rugate filters were filled with different ionic liquids yielded unique responses to organic vapors when decreases in peak intensity across the array were analyzed via principal component analysis (PCA). A number of these studies focused on using one PhC as a reference channel. For example, Ruminski et al. used a rugate filter double-stack in which one stack was hydrophobic and one stack was hydrophilic, each stack with a different peak wavelength. After determining the weighted difference in peak shift of each stack when exposed to various water vapor concentrations, the response to an organic/water vapor mixture could be corrected to remove the contribution of humidity. While the authors note that the rugate filter double-stack was not selective to different organic vapor analytes, the study did show that the spectral response to water of a particular concentration was different for each surface. Similarly, a silicon rugate filter with an oxidized surface showed different organic vapor response trends when compared to a carbonized silicon rugate filter, presumably because of differences in interactions of the vapors with the surface. Despite these improvements, challenges remain in fabricating 1D porous silicon PhCs for sensitive, selective identification of a broad class of analyte vapors and mixtures that rivals the performance of natural PhCs.

In this work, an array-based approach to improve optical vapor selectivity was examined by analyzing spectra from two pSi silicon rugate filters with different surface functionalities, an ozone-oxidized surface and a carbonized surface. Each rugate filter was exposed separately to five different vapor concentrations of water, methanol (MeOH), ethanol (EtOH), dichloromethane (DCM), and dichloropentane (DCP). The spectra for a particular vapor concentration for each of the two substrates were then additively combined, resulting in improved selectivity to a particular analyte relative to the response of the individual rugate filters.

**RESULTS AND DISCUSSION**

The rugate sensors used in this study were prepared using the method developed by Kelly et al. In brief, a p-type silicon wafer was etched with hydrofluoric acid, yielding a substrate determined to be ~25 μm thick using the spectroscopic liquid infiltration method (SLIM). Films were then oxidized with ozone to provide a uniform silicon oxide surface prior to carbonization. A dilute furfuryl alcohol solution was applied to the substrate and catalyzed with oxalic acid to yield a poly(furfuryl alcohol) (PFA)-infiltrated pSi film. The film was then heated to produce a carbonized pSi sensor. Reflectance spectra of the oxidized pSi showed the characteristic peak of pSi rugate filters etched using a sinusoidally varying current. The wavelength of the peak was adjusted by altering the periodicity of the sinusoidal current to yield a peak centered at 641 nm. Carbonization of the pSi film caused a red shift in the stop band, yielding a peak centered at 667 nm. Figure 1 shows the reflectance spectra for the freshly etched and carbonized pSi films. The stop band shows a large decrease in intensity upon carbonization, and the Fabry–Pérot interference fringes are no longer visible. As noted by Kelly et al., the shift in the peak position for the carbonized pSi film is caused by changes in the effective refractive index of the system. The decrease in peak intensity and disappearance of the Fabry–Pérot interference fringes have previously been attributed to the strong light absorption of carbon within the pores of the pSi film.

![Figure 1. Reflectance spectra of the (a) oxidized (solid line) and (b) carbonized (dashed line) pSi surfaces used in this study.](https://dx.doi.org/10.1021/acsomega.0c02689)

The extent of carbon infiltration in the pSi template was qualitatively characterized by Fourier transform infrared (FTIR) spectroscopy. As shown in Figure 2, the spectra of the freshly etched pSi film showed characteristic bands assigned to the Si–H stretching modes at ~2100 cm⁻¹, which was no longer observed following ozone oxidation. The oxidized spectrum had a broad peak centered at 3290 cm⁻¹ from the terminal O–H stretching, which was no longer observed following carbonization.

![Figure 2. FTIR spectra of (a) freshly etched, (b) oxidized, and (c) carbonized pSi films. The freshly etched spectrum showed a characteristic Si–H stretching band at 2100 cm⁻¹, which was no longer observed following ozone oxidation. The oxidized spectrum had a broad peak centered at 3290 cm⁻¹ from the terminal O–H stretching, which was no longer observed following carbonization.](https://dx.doi.org/10.1021/acsomega.0c02689)
yielded 4.8% carbon by mass. The porous structures of freestanding oxidized and carbonized pSi rugate filters were characterized using nitrogen adsorption/desorption analysis. As shown in Figure 3, the bimodal desorption isotherm typically observed in carbonized pSi composites is not observed in either sample. This absence of a bimodal desorption isotherm for the carbonized substrate was not unexpected, as ethanol was used in this work to dilute the furfuryl alcohol, resulting in a lower carbon content relative to other studies. The hysteresis present in both the oxidized and carbonized pSi substrates indicates multilayer gas adsorption, followed by capillary condensation. The desorption slope for the oxidized pSi surface was consistent with a mesoporous substrate with high pore size uniformity, while the desorption slope for the carbonized pSi surface indicated a less uniform pore size and shape. There is a large initial decrease in the Barrett–Joyner–Halenda (BJH) pore diameter from 15.43 ± 0.08 nm for the ozone-oxidized substrate to 10.07 ± 0.26 nm for the carbonized substrate. Similar results were observed in the BJH pore volume. There is a large initial decrease from 0.90 cm$^3$ g$^{-1}$ for the oxidized pSi rugate filter to 0.55 cm$^3$ g$^{-1}$ for the carbonized pSi rugate filter. Collectively, these results suggest that the carbonization process yielded carbon within the pores of the pSi rugate filter, reducing the pore diameter, pore volume, and pore uniformity relative to the oxidized pSi rugate filter.

The spectral response of both the oxidized and the carbonized pSi rugate filters to a number of analyte vapors was tested separately using the instrumentation schematic shown in Figure 4. Nitrogen at a flow rate of 400 mL min$^{-1}$ was used to obtain a spectral baseline. An analyte vapor of a particular concentration was introduced into the measurement chamber by bubbling nitrogen through the liquid analyte. Digital mass flow controllers were used to keep a constant total flow rate of 400 mL min$^{-1}$.

Figure 3. Nitrogen adsorption (solid black circles) and desorption (solid gray diamonds) isotherms for the (a) oxidized and (b) carbonized silicon rugate filters used in this work.
within a data set. In Figure 6, each point on the PCA plot indicates the differential reflectance spectra for a particular analyte and concentration. Again, differential reflectance spectra ($\Delta R$) reports the percentage difference of the reflectance with the analyte relative to the nitrogen baseline without the analyte.37 Significant spacing between points of the same analyte indicates good sensitivity, while separation of analyte curves indicates good selectivity.39 Thus, Figure 6 shows a tested sensitivity down to $\sim 30$ ppm for DCP on both the oxidized and carbonized pSi substrates. Low ppm sensitivities of 1D pSi photonic crystals have been reported in a number of studies.21,27,28,40,41 Also similar to literature results, neither the oxidized nor carbonized pSi rugate filter individually demonstrated selectivity.38 As shown in Figure 6 for both pSi surfaces, all analytes generally fell along the same line, a product of refractive index and vapor concentration.11 However, the different trends of the analyte peak shift for the two pSi rugate filters (Figure 5c,d) suggested that a parallel examination of the data (e.g., an array-type data analysis) could lead to enhanced vapor selectivity.

Toward that end, the individual reflectance spectra for a particular analyte concentration for the oxidized and carbonized pSi substrates were additively combined. An example of this additive combination is shown in Figure 7a–c. PCA was then performed on this additive combination of spectra from the oxidized and the carbonized pSi rugate filters, the results of which are shown in Figure 7d,e. Comparing Figure 7d and Figure 6, selectivity improvements are apparent when the two data sets are analyzed together versus individually, as evidenced by the $y$-axis separation of analyte traces in Figure 7d relative to Figure 6. Additionally, even analytes that appear to potentially overlap in the two-dimensional PCA plot (Figure 7d) show good separation in the three-dimensional PCA plot (Figure 7e).

Based on similar studies, this increase in selectivity by spectral analysis from the two different pSi rugate filters is somewhat expected. A limited number of studies have used various functional coatings on 1D porous silicon and analyzed the resulting spectra in a number of ways, resulting in improved sensitivity. PCA of peak shifts and peak reflectance intensity from an array of 1D porous silicon substrates coated with different ionic liquids yielded selectivity to common organic vapors, though concentrations less than 0.20$P_0$ were not tested.24,25 Additionally, an array of functionalized silica and titania Bragg stacks exposed to organic vapors demonstrated selectivity when monitored for changes in pixels from color images of the array.12 Again, though, only high (e.g., saturated)
vapor concentrations were examined. Unique to the work presented here, though, an additive combination of the spectra of only two 1D pSi with different functionalities tested at low vapor concentrations (e.g., 0.02 \( P_0 \)) showed good sensitivity and selectivity. Indeed, the selectivity and sensitivity rival those of some natural photonic crystals when exposed to the same vapors and concentrations.\(^{36,37} \)

Further improvements to the sensitivity and selectivity of 1D pSi optical vapor sensors could be realized by a combination of a variety of methods to include aperiodic structures with high surface areas,\(^{43} \) optimized numbers and types of functional coatings,\(^{24,25} \) monitoring of multiple parameters to include additive spectra and color images,\(^{42} \) and optimized analysis techniques of multiparameter sensing methods based on machine learning. Notably, DCP is a mustard gas simulant, and the sensitivity and selectivity demonstrated in this work approach the useful range for mustard gas sensing.\(^{44} \) Combined with the other inherent advantages of 1D pSi, to include facile integration with electronics and other sensing mechanisms via conductivity, optical vapor sensing based on 1D pSi should be possible at a sensitivity and selectivity requisite for most environments, to include the homeland defense and battlespace operation communities.

### CONCLUSIONS

In summary, this work highlights a method to increase the optical vapor selectivity of 1D pSi photonic crystals by analyzing additive spectra from two pSi substrates with different surface functionalities. Individually, both pSi rugate filters demonstrated sensitivity but not selectivity toward the vapor analytes. However, differences in peak shift trends between the two surfaces suggested differences in vapor affinities for the surfaces. By adding the two spectra, improvements to selectivity relative to the individual surfaces were observed even at low vapor pressures and for analytes of similar polarity, refractive index, and concentration. These results are expected to contribute toward optical vapor selectivity improvements in 1D porous silicon that exceeds the performance of some natural systems.

### MATERIALS AND METHODS

**Materials.** Oxalic acid dihydrate (ACS grade, 247537), furfuryl alcohol (98%, 185930), and 1,5-dichloropentane (DCP, 99%, D69602) were purchased from Sigma-Aldrich. Ethanol (EtOH, ACS grade, 111000190), methanol (MeOH, ACS grade, 339000000), and dichloromethane (DCM, ACS grade, 313000ACSPL) were purchased from Pharmco-Aaper. Ultra-pure water (Milli-Q Gradient A-10, Milli-Q, 18.2 \( \Omega \) cm, <5 ppb organic impurities) and ultrahigh purity nitrogen (Airgas, UHP300) were used for all experiments.

**Porous Silicon Preparation. Reflectance Measurements.** Porous silicon samples were prepared from highly doped p-type silicon wafers (boron-doped, \( \rho = 0.845 \) m\( \Omega \) cm\(^{-1} \), (100) orientation, obtained from Virginia Semiconductor Inc.) by electrochemical anodization in a solution of 49% aqueous HF in absolute ethanol (3:1 v/v HF/ethanol). Silicon chips were etched using an aluminum foil backing and a platinum coil counter electrode in a Teflon cell with an exposed area of 8.6 cm\(^2 \). Porous silicon rugate filters were etched by applying a sinusoidally varying current density of 10–100 mA cm\(^{-2} \), with a period of 8 s for 100 cycles. Samples were rinsed with ethanol and dried under a stream of nitrogen gas. Freshly etched chips were cut into smaller samples measuring approximately 1.5 cm\(^2 \) and then oxidized in a flow of ozone gas (1.5 SCFH) for 20 min.

**Freestanding Substrates for Characterization.** Freestanding pSi porous membranes for elemental and Brunauer–Emmett–Teller (BET)/BJH analyses were prepared from highly doped p-type silicon (boron-doped, \( \rho = 1.26 \) m\( \Omega \) cm\(^{-1} \), (100) orientation, obtained from Virginia Semiconductor Inc.)
by electrochemical anodization in a solution of 49% aqueous HF in absolute ethanol (3:1 v/v HF/ethanol). Porous silicon rugate filters were etched by applying a sinusoidally varying current density of 10−100 mA cm−2 with a period of 6.67 s for 600 repetitions (HF solution was replaced every 100 repeats). The freshly etched pSi film was lifted off from the bulk underlying silicon substrate by replacing the etching solution with 3.3% HF in ethanol and etching at 50 mA cm−2 for 480 s. The freshly etched pSi film thickness was determined to be ~150 μm by SLIM.

Carbonized Porous Silicon Preparation. Reflectance Measurements. Carbon/pSi sensors used in this study were prepared using the method developed by Kelly et al.28 Freshly etched pSi films were oxidized for 20 min under a stream of ozone to provide a uniform silicon oxide surface prior to carbonization.30 Furfuryl alcohol solutions for carbonization of the oxidized films were prepared by diluting 100 μL of furfuryl alcohol with 900 μL of absolute ethanol and using 5 mg mL−1 oxalic acid to catalyze the polymerization process, yielding a poly(furfuryl alcohol) (PFA)-infiltrated pSi film.45 Films were heated at 50 °C for 30 min and then at 700 °C for 2 h to produce carbonized pSi sensors.

Freestanding Substrates for Characterization. Freestanding carbonized pSi membranes for elemental and BET/BJH analyses were prepared by immersing a freestanding pSi membrane into a 9:1 v/v ethanol/furfuryl alcohol solution catalyzed by oxalic acid, followed by heating at 50 °C for 30 min and then at 700 °C for 2 h.

Characterization. Infrared Spectroscopy. Fourier transform infrared (FTIR) spectroscopy was utilized to characterize the pore wall surface chemistry. Spectra were acquired on a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with an attenuated total reflectance (ATR) accessory.

Elemental Analysis. The carbon content of the carbonized pSi samples was determined on freestanding samples using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. Three trials were run per sample with masses between 2 and 3 mg each.

Nitrogen Adsorption/Desorption. The average pore diameter of freestanding samples was characterized via nitrogen adsorption—desorption isotherms obtained at 77 K using a Micromeritics ASAP 2020 instrument. The samples were degassed for 5 h at 250 °C prior to adsorption measurements. Pore dimensions were determined using the Brunauer–Emmett–Teller (BET) theory.46

Reflectance Measurements. Reflectance spectra were collected using a halogen light source (Ocean Optics, HL-2000) and a spectrometer (Ocean Optics, HR2000+) equipped with a bifurcated optical probe (Ocean Optics, QR400–7–UV/Vis). The optical probe was normal to the rugate filter surface, generating an illuminated area of about 2 mm in diameter. Vapor concentrations were varied by bubbling the nitrogen carrier gas at a particular flow rate into the analyte liquid so that the partial pressure of the analyte vapor was between 0.02P0 and 0.3P0, where P0 is the saturated vapor pressure at 20 °C. The total gas flow rate for all measurements was held constant at 400 mL min−1 by mass flow controllers (Alicat Scientific), and the temperature was held constant at 20 °C. The reflectance measurement cell had a volume of 500 mL, while the gas tubing had a total volume of 270 mL. Each spectrum was collected after 10 min of exposure to the vapor. Mild heating of the pSi rugate filter to 80 °C facilitated the rapid return of the spectra to the nitrogen baseline between analyte tests.28 For both pSi rugate filters, three separate runs of each analyte concentration were collected and averaged. Rather than a reflectance standard, differential reflectance spectra were collected and analyzed.6,11,37 PCA was performed on the averaged differential spectra relative to nitrogen after mean-centering the data.

AUTHOR INFORMATION

Corresponding Author

Joshua D. Kittle — Department of Chemistry and Chemistry Research Center, United States Air Force Academy, Colorado Springs, Colorado 80840, United States; orcid.org/0000-0002-7920-2814; Email: joshua_d.kittle@us.af.mil

Authors

John S. Gofus III — Department of Chemistry and Chemistry Research Center, United States Air Force Academy, Colorado Springs, Colorado 80840, United States
Andrea N. Abel — Department of Chemistry and Chemistry Research Center, United States Air Force Academy, Colorado Springs, Colorado 80840, United States
Benjamin D. Evans — Department of Chemistry and Chemistry Research Center, United States Air Force Academy, Colorado Springs, Colorado 80840, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02689

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Defense Threat Reduction Agency (DTRA)—Joint Science and Technology Transfer Officer for Chemical and Biological Defense (MIPR No. HDTRA13964) and the Air Force Office of Scientific Research (AFOSR).

REFERENCES

(1) Yablonovitch, E. Photonic band structure. J. Opt. Soc. Am. B 1993, 10, 283–295.
(2) Fenzl, C.; Hirsch, T.; Wölbbeis, O. S. Photonic crystals for chemical sensing and biosensing. Angew. Chem., Int. Ed. 2014, 53, 3318–3335.
(3) Levitsky, I. A. Porous silicon structures as optical gas sensors. Sensors 2015, 15, 19968–19991.
(4) Potyrailo, R. A.; Ghiradella, H.; Vertiatchikh, A.; Dovidenko, K.; Cournoyer, J. R.; Olson, E. Morpho butterfly wing scales demonstrate highly selective vapour response. Nat. Photonics 2007, 1, 123–128.
(5) Potyrailo, R. A.; Bonam, R. K.; Hartley, J. G.; Starkey, T. A.; Vukusic, P.; Vasudev, M.; Bunning, T.; Naik, R. R.; Tang, Z.; Palacios, M. A.; Larsen, M.; Le Tarte, L. A.; Grande, J. C.; Zhong, S.; Deng, T. Towards outperforming conventional sensor arrays with fabricated individual photonic vapour sensors inspired by Morpho butterflies. Nat. Commun. 2015, 6, No. 7959.
(6) 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, 5415–5421.
(7) Sailor, M. J. Porous Silicon in Practice; Wiley-VCH Verlag: Weinheim, Germany, 2012.
(8) Lees, I. N.; Lin, H.; Canaria, C. A.; Gurtner, C.; Sailor, M. J.; Miskelly, G. M. Chemical stability of porous silicon surfaces electrochemically modified with functional alkyl species. Langmuir 2003, 19, 9812–9817.
(9) Ruminski, A. M.; King, B. H.; Salonen, J.; Snyder, J. L.; Sailor, M. J. Porous silicon-based optical microsensors for volatile organic analytes:
effect of surface chemistry on stability and specificity. Adv. Funct. Mater. 2010, 20, 2874–2883.

(10) Oton, C. J.; Pancheri, L.; Gaburro, Z.; Pavesi, L.; Baratto, C.; Faglia, G.; Serbevoglieri, G. Multiparametric porous silicon gas sensors with improved quality and sensitivity. Phys. Stat. Sol. (A) 2003, 197, 523–527.

(11) Potyrailo, R. A.; Starkey, T. A.; Vukusic, P.; Ghiradella, H.; Vassudev, M.; Bunning, T.; Naik, R. B.; Tang, Z.; Larsen, M.; Deng, T.; Zhong, S.; Palacios, M.; Grande, J. C.; Zorn, G.; Goddard, G.; Zalubovsky, S. Discovery of the surface polarity gradient on iridescent Morpho butterfly scales reveals a mechanism of their selective vapor response. Proc. Natl. Acad. Sci. U.S.A. 2013, 110, 15567–15572.

(12) Snow, P. A.; Squire, E. K.; Russell, P. S. J.; Canham, L. T. Vapor sensing using the optical properties of porous silicon Bragg mirrors. J. Appl. Phys. 1999, 86, 1781–1784.

(13) Content, S.; Troger, W. C.; Sailor, M. J. Detection of nitrobenzene, DNT, and TNT vapors by quenching of porous silicon photoluminescence. Chem. – Eur. J. 2000, 6, 2205–2213.

(14) Sailor, M. J.; Wu, E. C. Photoluminescence-based sensing with porous silicon films, microparticles, and nanoparticles. Adv. Funct. Mater. 2009, 19, 3195–3208.

(15) Bakker, J. W. P.; Arwin, H.; Wang, G.; Järrendahl, K. Improvement of porous silicon-based gas sensors by polymer modification. Phys. Stat. Sol. A. 2003, 197, 378–381.

(16) Sohn, H.; Létant, S.; Sailor, M. J.; Troger, W. C. Detection of fluorophosphonate chemical warfare agents by catalytic hydrolysis with porous silicon interferometer. J. Am. Chem. Soc. 2000, 122, 5399–5400.

(17) Létant, S.; Sailor, M. J. Detection of HF gas with a porous silicon interferometer. Adv. Mater. 2000, 12, 355–359.

(18) Karlsson, L. M.; Schubert, M.; Ashkenov, N.; Arwin, H. Protein adsorption in porous silicon gradient monitored by spatially-resolved spectroscopic ellipsometry. Thin Solid Films 2004, 455-456, 726–730.

(19) Collins, B. E.; Dancil, K.-P. S.; Abbi, G.; Sailor, M. J. Determining protein size using an electrochemically machined pore gradient in silicon. Adv. Funct. Mater. 2002, 12, 187–191.

(20) King, B. H.; Wong, T.; Sailor, M. J. Detection of pure chemical vapors in a thermally cycled porous silica photonic crystal. Langmuir 2011, 27, 8576–8585.

(21) Kelly, T. L.; Sega, A. G.; Sailor, M. J. Identification and quantification of organic vapors by time-resolved diffusion in stacked mesoporous photonic crystals. Nano Lett. 2011, 11, 3169–3173.

(22) King, B. H.; Gramada, A.; Link, J. R.; Sailor, M. J. Internally referenced ammonia sensor based on an electrochemically prepared porous SiO2 photonic crystal. Adv. Mater. 2007, 19, 4044–4048.

(23) Sweetman, M. J.; Voelcker, N. H. Chemically patterned porous silicon photonic crystals towards internally referenced organic vapor sensors. RSC Adv. 2012, 2, 4620–4622.

(24) Shang, Y.; Zhang, H.; Wang, X.; Wu, J. An optical olfactory sensor based on porous silicon infiltrated with room-temperature ionic liquid arrays. Chem. – Eur. J. 2011, 17, 13400–13404.

(25) Zhang, H.; Lin, L.; Liu, D.; Chen, Q.; Wu, J. Optical nose based porous silicon photonic crystal infiltrated with ionic liquids. Anal. Chem. Acta 2017, 753, 71–78.

(26) Murguía, J. S.; Vergara, A.; Vargas-Olmos, C.; Wong, T. J.; Fonollosa, J.; Huerta, R. Two-dimensional wavelet transform feature extraction for porous silicon chemical sensors. Anal. Chem. Acta 2013, 785, 1–15.

(27) Ruminski, A. M.; Moore, M. M.; Sailor, M. J. Humidity-compensating sensor for volatile organic compounds using stacked porous silicon photonic crystals. Adv. Funct. Mater. 2008, 18, 3418–3426.

(28) Kelly, T. L.; Gao, T.; Sailor, M. J. Carbon and carbon/silicon composites templated in rugate filter for the adsorption and detection of organic vapors. Adv. Mater. 2011, 23, 1776–1781.

(29) Korotcenkov, G.; Rasu, E. How to improve the performance of porous silicon-based gas and vapor sensors? Approaches and achievements. Phys. Status Solidi A 2019, 216, No. 1900348.

(30) King, B. H.; Ruminski, A. M.; Snyder, J. L.; Sailor, M. J. Optical-fiber-mounted porous silicon photonic crystals for sensing organic vapor breakthrough in activated carbon. Adv. Mater. 2007, 19, 4530–4534.

(31) Bertarione, S.; Bonino, F.; Cesano, F.; Damin, A.; Scarano, D.; Zecchina, A. Furfuryl alcohol polymerization in H-Y confined spaces: reaction mechanism and structure of carbocationic intermediates. J. Phys. Chem. B 2008, 112, 2580–2589.

(32) Berger, M. G.; Arens-Fischer, R.; Thöniessen, M.; Krüger, M.; Billat, S.; Lüth, H.; Hilbrich, S.; Theiß, W.; Grosse, P. Dielectric filters made of PS: Advanced performance by oxidation and new layer structures. Thin Solid Films 1997, 297, 237–240.

(33) Canaria, C. A.; Lees, I. N.; Wun, A. W.; Miskelly, G. M.; Sailor, M. J. Characterization of the carbon-silicon stretch in methylated porous silicon – observation of an anomalous isotope shift in the FTIR spectrum. Inorg. Chem. Commun. 2002, 5, 560–564.

(34) Chan, D. Y.; Sega, A. G.; Lee, J. Y.; Gao, T.; Cunin, F.; Renzo, F. D.; Sailor, M. J. Optical detection of C2 hydrocarbons ethane, ethylene, and acetylene with a photonic crystal made from carbonized porous silicon. Inorg. Chim. Acta 2014, 422, 21–29.

(35) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierrotti, R. A.; Rouquéroil, J.; Siemieniewska, T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl. Chem. 1985, 57, 603–619.

(36) Kittle, J. D.; Fisher, B. P.; Esparza, A. J.; Morey, A. M.; Iacono, S. T. Sensing chemical warfare agent simulants via photonic crystals of the Morpho didius butterfly. ACS Omega 2017, 2, 8301–8307.

(37) Kittle, J. D.; Fisher, B. P.; Kunselman, C.; Morey, A. M.; Abel, A. N. Vapor selectivity of a natural photonic crystal binary and tertiary mixtures containing chemical warfare agent simulants. Sensors 2020, 29, 20177.

(38) Wu, C.-C.; Chen, M. Y.; Sailor, M. J. Differential adsorption of small molecules in spatially functionalized porous silicon nanostructures. Langmuir 2013, 29, 11802–11808.

(39) Potyrailo, R.; Naik, R. R. Bionanomaterials and bioinspired nanostructures for selective vapor sensing. Annu. Rev. Mater. Res. 2013, 43, 307–334.

(40) Salem, M. S.; Sailor, M. J.; Fukami, K.; Sakka, T.; Ogata, Y. H. Sensitivity of porous silicon rugate filters for chemical vapor detection. J. Appl. Phys. 2008, 103, No. 083516.

(41) Kim, S.; Cho, B.; Sohn, H. Detection of nerve agent stimulants based on photoluminescent porous silicon interferometer. Nanoscale Res. Lett. 2012, 7, 527.

(42) Bonifacio, L. D.; Puzo, D. P.; Breslau, S.; Willey, B. M.; McGeer, A.; Ozin, G. A. Towards the photonic nose: a novel platform for molecule and bacteria identification. Adv. Mater. 2010, 22, 1351–1354.

(43) Moretti, L.; Rea, I.; De Stefano, L.; Rendina, I. Periodic versus aperiodic: enhancing the sensitivity of porous silicon based optical sensors. Appl. Phys. Lett. 2007, 90, No. 191112.

(44) Jeong, Y.; Kim, K.; Tsay, O. G.; Atwood, D. A.; Churchill, D. G. Update 1 of: destruction and detection of chemical warfare agents. Chem. Rev. 2015, 115, PR1.

(45) Bertarione, S.; Bonino, F.; Cesano, F.; Damin, A.; Scarano, D.; Zecchina, A. Furfuryl alcohol polymerization in H-Y confined spaces: reaction mechanism and structure of carbocaticonic intermediates. J. Phys. Chem. B 2008, 112, 2580–2589.

(46) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 1938, 60, 309–319.