

Organic Solvent Vapor Detection Using Holographic Photopolymer Reflection Gratings**

By Vincent K. S. Hsiao, William D. Kirkey, Fei Chen, Alexander N. Cartwright,* Paras N. Prasad, and Timothy J. Bunning

Significant research efforts have focused on the development of effective means for the detection of organic molecules. These efforts can be divided, very crudely, into those focusing on either electrical- or optical-sensing mechanisms. To date, sensors based on optical measurements have generally proven to be faster, safer, and easier to implement than those employing electrical measurements.^[1] In particular, porous materials are well suited for use as templates for optical sensing. Porous silicon is an especially appealing material for these applications due largely to the fact that it can be readily structured using electrochemical etching and/or photolithography. For example, highly reflective porous silicon microcavities can be generated by using controlled etching, resulting in layers of alternating porosities.^[2,3] Recently, excellent progress has been made in creating porous silicon films,^[4,5] microcavities,^[6,7] and arrays of microstructures^[8] useful for optical sensing. Generally, these devices rely on the changes in the optical resonance that occur when the porous structure is occupied by the analyte species, allowing for simple and effective detection schemes. However, the versatility of porous silicon is tempered by its instability. As an alternative, porous polymer nanostructures produced from an oxidized porous silicon template have been demonstrated as a way for sensing applications.^[9] Micropatterned polymeric gratings have also been demonstrated as a relevant sensing material for detecting organic solvents. For example, instead of using a porous layer-by-layer geometry of a reflection grating, a micropatterning transmission grating (array design) was shown to have the ability to identify a mixture of chemical analytes.^[10] In the work reported in this communication, we demonstrate a simple method for optical detection of different or-

ganic-solvent vapors based on the holographic fabrication of high-porosity polymer Bragg reflection gratings. Furthermore, these results demonstrate that this photopolymer fabrication technique could potentially be used to create structures suitable for biological applications in aqueous environments.

The typical method used to produce periodic porous silicon structures is relatively complicated, requiring a controlled electrochemical etching process in a hydrofluoric acid solution.^[1–3,5–9] In contrast, it has recently been demonstrated that organic polymeric materials can yield high-efficiency reflection gratings through a fast and inexpensive holographic photopolymerization technique.^[11] In this technique, a prepolymer syrup containing a monomer, a photoinitiator, a co-initiator, and a liquid crystal (LC) is sandwiched between two pieces of glass, and a periodic structure is then formed by applying an optical interference pattern generated using a simple one-beam setup.^[12] We have recently demonstrated that porous acrylate polymer grating structures can be created in a similar manner by simply adding a non-reactive solvent, such as acetone or toluene, into the prepolymer syrup prior to photopolymerization.^[13] In this case, the grating appears when the non-reactive solvent evaporates upon exposing the polymerized film to air. The porosity of the final structure can be controlled by varying the composition of the initial prepolymer syrup and experimental conditions. Figure 1 shows the morphology of a typical porous polymer grating structure, observed using bright-field transmission electron microscopy (BFTEM). In this case, the white regions are air voids (refractive index, $n_{\text{air}} = 1.0$) while the black regions are polymer ($n_{\text{p}} = 1.52$), and the porosity of the grating structure is determined to be approximately 30 %.

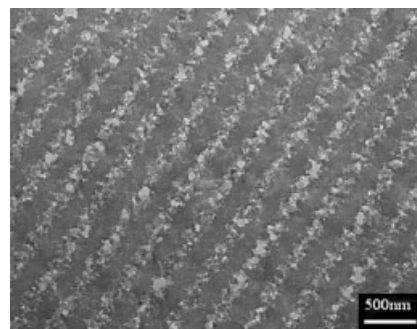


Figure 1. BFTEM image of the grating structure.

The Bragg reflection notch of these gratings can then be shifted by filling the voids inside the grating structure with solvent vapor. This changes the average refractive index of the material, modifying the grating's behavior according to the formula

$$\lambda_{\text{Bragg}} = 2 n_{\text{ave}} \Lambda \quad (1)$$

where λ_{Bragg} is the reflected wavelength, n_{ave} is the average refractive index of the grating film, and Λ is the grating spacing. The chemical vapors can easily permeate into the voids in the

[*] Prof. A. N. Cartwright, V. K. S. Hsiao, W. D. Kirkey, Dr. F. Chen, Prof. P. N. Prasad
Department of Electrical Engineering
Institute for Lasers, Photonics and Biophotonics
University at Buffalo, The State University of New York
Buffalo, NY 14260-3000 (USA)
E-mail: anc@buffalo.edu

Dr. T. J. Bunning
Air Force Research Laboratory, Materials and Manufacturing
Directorate
Wright-Patterson Air Force Base, OH 45433-7500 (USA)

[**] This work was supported by the Air Force Office of Scientific Research (Defense University Research Initiative on Nanotechnology Grant #F469200110358) and in part by the National Science Foundation (Integrative Graduate Education and Research Traineeship #DGE0114330). The authors thank Prof. Mark Swihart for helpful discussions.

grating film and consequently change the average refractive index and the corresponding reflective wavelength. These changes in optical response can be readily observed due to the large index difference between the air voids ($n_{\text{air}} = 1$) and the chemical vapor (normally > 1.36). Thus, these holographic porous polymer gratings can act as colorimetric vapor sensors.

Figure 2 shows the transmission spectrum of a grating cell in air with different concentrations of acetone vapor present. An increase in the concentration of the acetone vapor changed the average index of the grating, consequently in-

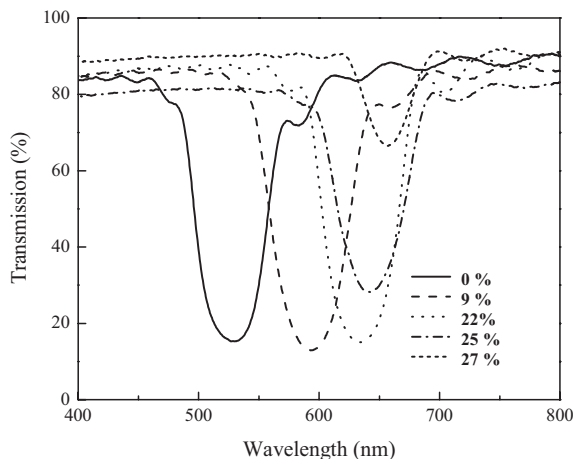


Figure 2. The transmission spectra of a typical grating film in air containing various concentrations of acetone vapor (vol.-%) relative to 1 atm (101.325 kPa) air pressure.

creasing the effective grating spacing. Other chemical vapors including methanol, chloroform, pyridine, and toluene have also been tested, and similar optical responses were obtained. The porous polymer grating sensor here offers a way to measure the changes in the concentration of a known chemical solvent using the naked eye. Figure 3 shows the optical response of a porous grating structure to different analytes of organic vapor in the same percentage (9 vol.-%) of concentration. In these cases, the Bragg wavelength of the grating red shifts from 630 nm to 650, 660, and 670 nm; the full width at half maximum (FWHM) narrows from 90 nm to 70, 60, and 50 nm; and the diffraction efficiency changes from 70 % to 65, 60, and 45 % for acetone, chloroform, and toluene, respectively. More importantly, through chemical modification of the polymer or exposed surfaces of the resulting structure, it should be possible to make these changes occur for specific chemical vapors of interest.

We note that the wavelength shifts observed in these structures are far too large to be explained simply by the displacement of air in the pores by condensed acetone, as occurs in analogous porous-silicon vapor sensors.^[6] According to the Bragg equation, and assuming a polymer refractive index of about 1.5, a structure with a 200 nm grating spacing and 40 % porosity would exhibit a wavelength shift of only about 60 nm if the pores were completely filled with liquid acetone

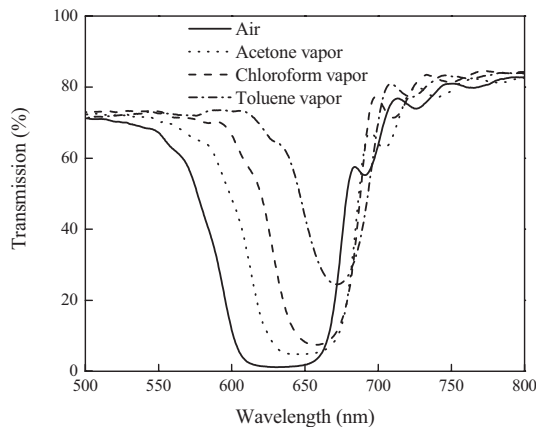


Figure 3. The spectral response for a grating film upon exposure to different analytes in the same percentage (9 vol.-%) of vapor pressure; $n_{\text{acetone}} = 1.36$, $n_{\text{chloroform}} = 1.45$, and $n_{\text{toluene}} = 1.50$.

($n_{\text{acetone}} = 1.36$). This suggests that there is another reversible mechanism occurring that affects the optical thickness $n_{\text{ave}} \Delta$ of the gratings. One possible cause for this could be absorption of acetone solvent by the polymer, which would cause the grating to swell, increasing the physical grating spacing. Liquid acetone uptake has been shown to substantially swell photochemically crosslinked poly(*n*-butylacrylate), increasing the diameter of the polymer network by about 80%.^[14] Such swelling could explain the dramatic wavelength shifts observed in Figure 2.

Figure 4 shows the cycling behavior of the sample exposed under alternative concentrations of acetone vapor. The observation wavelength for these measurements was 600 nm, and this wavelength corresponded to the central wavelength of the

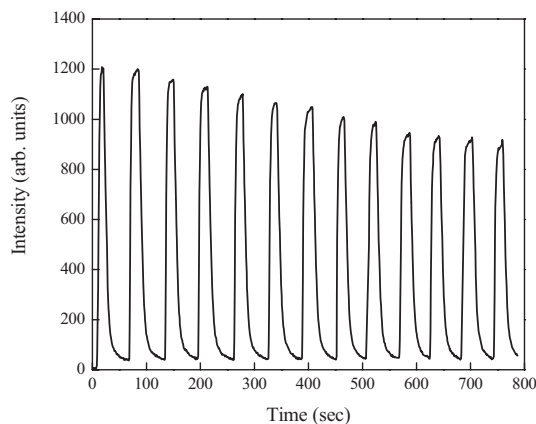


Figure 4. Cycling behavior of the grating. The film was subjected to alternating acetone vapor from 0.2 to 1 mbar (0.02 to 0.1 Pa).

transmission spectrum. When the acetone vapor (mixed with air) is added to the chamber, the peak reflection wavelength shifts towards longer wavelengths and the observed intensity at 600 nm increases. Once the chamber pressure exceeds

1 mbar (0.1 Pa), the intensity reaches its maximum and the film becomes transparent at 600 nm. After ~30 s, the valve of the vacuum pump was opened, restoring the vacuum, and the transmission signal decreases as the vacuum decreased to 0.2 mbar (0.02 Pa). This reversibility indicates that there is no chemical interaction between the vapor and the polymeric structure. It was found that the cycling effect degrades the measured response of the sample by ~20% after 10 cycles.

One initial drawback to the polymer/LC composite-based reflection gratings described above is the long-term instability of the porous polymer. When stored in air, the film generally peeled away from the substrate within a few months. Even more seriously, the film was easily washed from the glass by water. Finally, under certain conditions, the polymer film would sometimes crack when the cover glass was removed due to surface tension that developed between the polymer and the glass as the solvent evaporated. However, all of these problems were easily overcome by adding a small amount of the silane compound, 3-aminopropyltriethoxysilane, to the prepolymer syrup. This strongly enhances the contact between the polymer and the glass, while not adversely affecting grating formation. In contrast, without the silane compound present, the sample would easily delaminate from the glass substrate when immersed in water. It should be noted that 3-aminopropyltriethoxysilane is commonly used for preparing amino functional surfaces on glass and silica. This suggests that use of this compound could aid in producing porous polymer gratings useful for biosensing applications, both by rendering such devices hydrophobic and by providing an amino functional group within the porous composite that could potentially be used to target protein analytes.

In conclusion, we have successfully produced a chemical-vapor sensor based on a porous polymer grating fabricated by holographic formation in a photopolymer system. The porous polymer film was easily filled with and cleared of the chemical vapors without damaging the grating structure. Therefore, changes in the refractive index and the effective grating spacing of the film could be readily and repeatedly observed. The sensing process was reversible and reliable, and could be observed either by the naked eye or by the detection of transmitted light. Thus, the use of holographic porous polymer reflection gratings provides an inexpensive and easy means to detect a chemical reagent. This work demonstrates the sensing ability of the porous polymer grating structures. It is envisioned that, by chemically modifying the surface of the pores or specifically adding different chemical species into the prepolymer syrup, one should be able to modify the chemical properties of the grating films and make this holographic fabrication suitable for different sensing applications.

Experimental

Sample Fabrication: Multilayer grating structures were prepared by a holographic technique using photopolymer syrups (60 wt.-%) composed of monomer (dipentaerythritol hydroxypentaacrylate), photoinitiator (Rose Bengal), co-initiator (*N*-phenylglycine), crosslinking

monomer (*N*-vinylpyrrolidinone), liquid crystal (TL213), and non-reactive solvent (toluene) (20 wt.-%). For the sample with silane incorporated, the toluene contained 1.5 wt.-% 3-aminopropyltriethoxysilane. The liquid crystal was commercially available from Merck; the photoinitiator was obtained from Spectra Group Limited; all other chemicals were obtained from Aldrich. The prepolymer syrup was mixed to ensure homogeneity with a mixer and a sonicator and then sandwiched between two glass slides. Holography was performed using the 514 nm line of an Ar ion laser with 100 mW of power; the exposure time was 30 s. The writing procedure was performed using a single-beam geometry, wherein the interference pattern was created between the incident beam and its total internal reflection from a prism [10]. After laser exposure, the sandwiched cell was post-cured under a 75 W lamp for 24 h. The reflection notch could be observed after removing the glass cover slide from the cell and allowing the incorporated solvent to evaporate [12].

Morphology and Optical Data Acquisition: The grating morphology was observed using a FEI CM200FEG transmission electron microscope operated in bright-field mode. The vapor-sensing measurement was performed by placing the grating sample inside a standard 10 mm × 10 mm × 50 mm rectangular spectrophotometer cell with a screw cap and septum on the top. The acetone vapor was injected into the spectrophotometer cell using a syringe, and the transmission spectra were acquired by a Shimadzu UV-VIS 3101PC spectrometer at different acetone-vapor concentrations. The concentration of acetone vapor was approximated based on the vapor pressure of acetone at room temperature. The housing, used to study the switching ability of the grating film, consisted of a stainless-steel vacuum chamber equipped with two optical windows and fitted with a mechanical vacuum pump and a vacuum gauge. The source of acetone vapor was a glass flask containing liquid acetone. The vacuum chamber was first evacuated to a vapor pressure of about 0.2 mbar (0.02 Pa), after which the valve connecting the chamber to the vacuum pump was closed. The valve linking the acetone flask to the chamber was then used to bring the chamber pressure to 1 mbar (0.1 Pa). In this manner, the acetone vapor filling and evacuation process were controlled using these two valves. The transmission spectrum was recorded by illuminating the sample with the collimated output of a white-light source, and directing the transmitted light through the optical access windows to a StellarNet EPP20000-C spectrometer on the opposite side of the chamber. The light passed at normal incidence through the grating sample in the chamber.

Received: November 17, 2004

Final version: April 13, 2005

Published online: August 16, 2005

- [1] V. Mulloni, L. Pavesi, *Appl. Phys. Lett.* **2000**, *76*, 2523.
- [2] M. G. Berger, C. Dieker, M. Thonissen, L. Vescan, H. Luth, H. Munder, W. Thieb, M. Wernke, P. Grosse, *J. Phys. D: Appl. Phys.* **1994**, *27*, 1333.
- [3] C. Mazzoleni, L. Pavesi, *Appl. Phys. Lett.* **1995**, *67*, 2983.
- [4] V. S. Y. Lin, K. Motesharei, K. P. S. Dancil, M. J. Sailor, M. R. Ghadiri, *Science* **1997**, *278*, 840.
- [5] J. Gao, T. Gao, Y. Y. Li, M. J. Sailor, *Langmuir* **2002**, *18*, 2229.
- [6] P. A. Snow, E. K. Squire, P. S. J. Russel, L. T. Canham, *J. Appl. Phys.* **1999**, *86*, 1781.
- [7] S. Chan, Y. Li, L. J. Rothberg, B. L. Miller, P. M. Fauchet, *Mater. Sci. Eng., C* **2001**, *15*, 277.
- [8] F. Cunin, T. A. Schmedake, J. R. Link, Y. Y. Li, J. Koh, S. N. Bhatia, M. J. Sailor, *Nat. Mater.* **2002**, *1*, 39.
- [9] Y. Y. Li, F. Cunin, J. Link, T. Gao, R. E. Betts, S. H. Reiver, V. Chin, S. N. Bhatia, M. J. Sailor, *Science* **2003**, *299*, 2045.
- [10] R. C. Bailey, J. T. Hupp, *Anal. Chem.* **2003**, *75*, 2392.
- [11] T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, *Annu. Rev. Mater. Sci.* **2000**, *30*, 83.

- [12] L. V. Natarajan, C. K. Shepherd, D. M. Brandelik, R. L. Sutherland, S. Chandra, V. P. Tondiglia, D. Tomlin, T. J. Bunning, *Chem. Mater.* **2003**, *15*, 2477.
- [13] V. K. S. Hsiao, T. C. Lin, G. S. He, A. N. Cartwright, P. N. Prasad, L. V. Natarajan, V. P. Tondiglia, T. J. Bunning, *Appl. Phys. Lett.* **2005**, *86*, 131 113.
- [14] T. Bouchaour, F. Benmouna, X. Coqueret, M. Benmouna, U. Mashke, *J. Appl. Polym. Sci.* **2004**, *91*, 1.

Silicate Glasses with Unprecedented High Nitrogen and Electropositive Metal Contents Obtained by Using Metals as Precursors**

By Abbas S. Hakeem, Rachel Daucé, Ekaterina Leonova, Mattias Edén, Zhijian Shen, Jekabs Grins, and Saeid Esmailzadeh*

A novel glass-synthesis route involving the reaction of electropositive elements in their metallic state with Si_3N_4 and SiO_2 in N_2 atmosphere is presented. New silicate glass compositions have been obtained in this way with nitrogen contents higher than 70 e/o (N content in equivalents; $e = [\text{N}] / 3[\text{N}] + 2[\text{O}]$, where $[\text{N}]$ and $[\text{O}]$ are the atomic concentrations of N and O, respectively), compared to previously reported oxynitride glasses typically that have concentrations below 30 e/o.^[1–8] The new glasses constitute a significant extension of silicate glass compositions and also show high chemical flexibility. Samples have been prepared with high concentrations of alkaline-earth and rare-earth elements such as Ca, Sr, Ba, La, Pr, and Sm (higher than 50 % cations; hereafter cation %). The glasses can easily be obtained in macroscopic quantities. They demonstrate high refractive indices, up to 2.30, and Vickers hardness values up to 13.3 GPa, which are the highest values reported for any silicate glass.

The technological use of silicate glasses constitutes an important part of modern civilization. They have, however, inherent compositional limitations that inhibit further improve-

ments of their various properties, e.g., the attainable amount of network-modifier elements (Na, Ca, Ba, etc.) is rather small and restricted by the Si/O ratio. One way of increasing the amount of electropositive elements in silicates is to substitute oxygen with nitrogen. Such oxonitridosilicates do not occur in nature and investigations of them originated from efforts to prepare new Si_3N_4 -based ceramic materials with improved mechanical properties, i.e. sialons.^[1–4] Sialon and oxonitridosilicate crystal chemistries are similar to that of oxosilicates, but differ in that nitrogen, unlike oxygen, may bond to three or even four Si atoms,^[5,6] resulting in higher connectivity and condensation of the networks. Due to the high formal charge of -3 for nitrogen, more or higher valent cations can be incorporated in the phases for a given network connectivity.

Studies of oxynitride glasses over the last few decades^[7–14] have demonstrated that an increase in nitrogen content increases the glass-transition temperature, T_g , viscosity, elastic modulus, hardness, and refractive index.^[6,15–17] This can be partly attributed to a higher crosslinking of the Si(Al) network. Increased nitrogen contents have been desired by both academic and industrial sectors to improve physical properties, but efforts so far have had limited success. The glass modifiers have mainly been added as oxides,^[1–7] typically leading to nitrogen contents less than 30 e/o.

In the synthesis method presented here, rare-earth and/or alkaline-earth elements are introduced instead as metals. Precursor mixtures of electropositive elements, Si_3N_4 , and SiO_2 , are ground in an oxygen- and water-free atmosphere and then heat treated, using graphite or radiofrequency furnaces, at 1500–1800 °C in N_2 atmosphere, which serves as the nitridation source for the metals. We have accordingly prepared glasses with significantly higher nitrogen contents than previously reported (varying between 35 and 70 e/o), which exhibit enhanced optical and mechanical properties. During synthesis, the electropositive metal reacts at a comparatively low temperature with the N_2 gas and forms a nitride without surface oxide layer, and is thus very reactive. Above ca. 1000 °C, it reacts with SiO_2 (the oxygen source), and then with the usually inert Si_3N_4 . A melt containing Si, O, N, and the electropositive element is then formed that dissolves the remaining SiO_2 and Si_3N_4 . The final melt is then cooled below T_g , using cooling rates less than 10 °C s⁻¹. The Si in the network can be partially replaced by trivalent B or Al by adding BN or AlN to the starting mixtures.

Compositions of the synthesized glasses in the system Ca–Si–O–N are given in Figure 1. A tendency of the materials to partially crystallize was observed for samples with Ca and N contents higher than 50 and 70 e/o, respectively. In view of a report of a binary Si_3N_4 – SiO_2 glass, obtained by quenching a melt from 1850 °C,^[18] it is likely that the vitreous zone boundaries in the present system are not only dependent on composition but also on preparation temperature and quench rate, the former being restricted by the dissociation of SiO_2 and Si_3N_4 at higher temperatures.^[18–20] The variation of T_g and crystallization temperature, T_c , with nitrogen content is shown

[*] Dr. S. Esmailzadeh, A. S. Hakeem, Dr. R. Daucé, Dr. J. Grins, Dr. Z. Shen
Department of Inorganic Chemistry, Arrhenius Laboratory
Stockholm University, SE-106 91 Stockholm (Sweden)
E-mail: zaida@inorg.su.se
E. Leonova, Dr. M. Edén
Department of Physical Chemistry, Arrhenius Laboratory,
Stockholm University, SE-106 91 Stockholm (Sweden)

[**] The authors are grateful to Professor Mats Nygren and Professor Sven Lidin for valuable discussions and Zheng Weng for technical NMR support. The Swedish Research Council (VR), the Swedish Agency for Innovation Systems (VINNOVA), the Swedish Foundation for Strategic Research (SSF), and the Carl Trygger Foundation (CTS) have financially supported this work. Supporting Information is available online from Wiley InterScience or from the author.