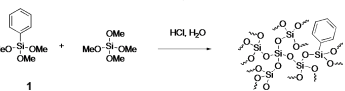


# ORGANOSILICATE FILMS COUPLED TO PHOTONIC BAND GAP MULTILAYER MATERIALS FOR GAS SENSING

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## Organosilicate Materials

Imprinted materials have broad applications including sensors, enantioselective materials, filters, and catalysts.<sup>1</sup> In this project we are exploring organically-modified silicate (ormosil) thin films and organosiloxanes as gas sensors. Ormosils are hybrid materials resulting from sol-gel processing of orthosilicates and mixtures of organosilanes. Our materials synthesis methodology relies on the work of Marx *et al.*<sup>2,3</sup> which incorporates 20% of functionalized organosilanes into a silicate matrix.



The organosilanes were chosen to mimic the polarity of the template so that imprinted nanocavities could be selective for a desired analyte. In this case, the analyte was 2,4-dinitrotoluene (DNT), a model for trinitrotoluene (TNT). These and common explosives are pictured below along with Figure 1, an idealized nanocavity.

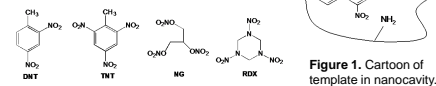


Figure 1. Cartoon of template in nanocavity.

## PBG Multilayer Materials

Ultimately, the sensor platform used to detect entrapped molecules will be a multilayered photonic bandgap material (PBGM),<sup>4</sup> a material that creates surface optical waves (SOWs), optical modes that propagate at the surface of the PBGM (Figure 2).

Light incident at an appropriate angle in a PBGM material creates an evanescent EM field in the vicinity of the surface that can couple to surface plasmons (SP). When coupling occurs, incident light is converted to SPs and there is a reduction in the reflected light. The reflectivity dip as a function of incident angle is the hallmark of coupling to SPs. Figure 3 demonstrates the increased sensitivity of PBGM over metals to the angular position of this reflectivity dip.

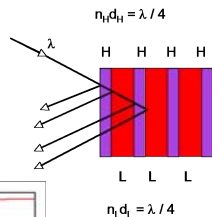


Figure 2. Substrate multilayer design, where high index material (H) is TiO<sub>2</sub> and low index (L) is SiO<sub>2</sub>, d is thickness and n is refractive index.

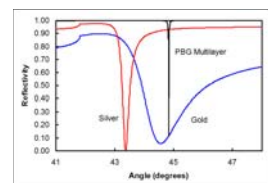


Figure 3. Dependence of reflectivity on angle for metals vs. PBGM layers.

## PBG Sensors

The sensor is based on detecting the change in resonance conditions when various entities bind within a material at the interface of the PBGM. The material/PBGM interface is shown in Figure 4. For optical analysis, the sample is placed within a portable flow cell device (Figure 5).

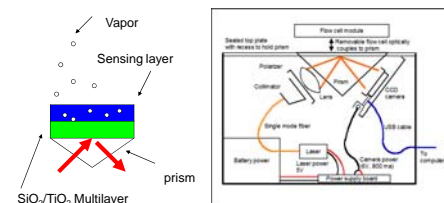


Figure 4. The materials interface containing nanocavities.

Figure 5. Portable device design with "flow cell" module for exposure of sample to vapor.

The unique aspect of the sensor design described here is that the organosilane-containing sensing layer is incorporated into the final layer of the PBGM. As a result, the sensitivity to changes in refractive index of the ormosil as it adsorbs analytes is expected to be high. A calculation of sensitivity of a model film, OV-225 to RI changes is shown in Figure 6. For comparison, the SEW penetration into the interface between the PBGM layer and air is shown in Figure 7. The blue line shows the area where analytes can be detected at highest sensitivity in <50 nm thick films, and the red line indicates sensitivity in a PBGM designed for <50 nm thick films.

Figure 6. Calculated angular mode shift for 0.01% (blue line), 0.1% (black line), and 1% (green line) changes in refractive index in a 700 nm thick OV-225 film.

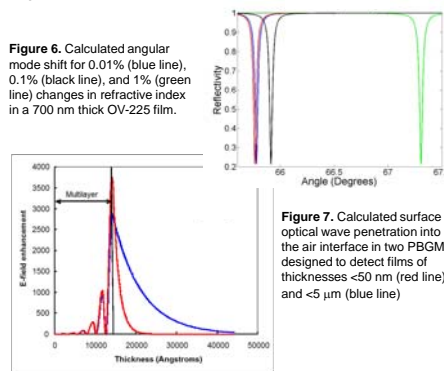


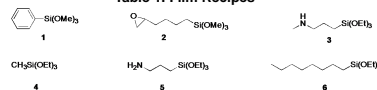
Figure 7. Calculated surface optical wave penetration into the air interface in two PBGM designed to detect films of thicknesses <50 nm (red line) and <5 μm (blue line).

## Other Sensing Platforms

Several sensors designed for trace explosives detection utilize fluorescence-based detection, thermal desorption, or GC/MS.<sup>5</sup> We will compare our experimental sensitivities using the PBGM-SOW techniques to data from these other sensing platforms.

## Film Synthesis and Properties

Table 1. Film Recipes



Recipe <sup>a</sup>	TMOS	TEOS	PTMOS	Silane (#)	HCl	Water	Ethanol	Time (h)
A	2.00	-	0.50	1	0.66 <sup>b</sup>	0.66	2.00 <sup>c</sup>	2
B	3.00	-	0.20	2, 0.16	1.00 <sup>b</sup>	1.00	5.87	2
C	-	3.00	0.20	3, 0.23	0.10	1.00	3.00	2-5
D	-	3.00	0.20	6, 0.23	0.10	1.00	3.00	5
E	-	3.00	0.20	5, 0.20	0.10	1.00	3.00	2-24
F	3.00	-	0.37	4, 0.51	1.00 <sup>b</sup>	1.00	3.00	2
G	3.00	-	0.37	4, 0.51	1.00 <sup>b</sup>	1.00	3.00	2

<sup>a</sup>All reagents in mL; <sup>b</sup> 0.1M HCl; <sup>c</sup> ethoxyethanol; <sup>d</sup> 1-dodecylpyridinium chloride hydrate; <sup>e</sup> 1-butanol.

Table 2. Film Thickness and Contact Angles

Film	Thickness (Ellipsometric, nm)	Thickness (Profilometric, nm)	Water Contact Angle θ (adv)(rec)
E	767 ± 1	775 ± 1	68 ± 2 / 64 ± 1
A	651 ± 4	711 ± 1	66 ± 2 / 64 ± 1
B	749 ± 11	774 ± 1	62 ± 1 / 61 ± 2
A	690 ± 2	707 ± 1	72 ± 2 / 60 ± 3
C	623 ± 1	608 ± 1	73 ± 1 / 52 ± 2

**Film thickness and hydrophobicity.** A Veeco profilometer and Woolham M-2000 Spectrometric Ellipsometer were used to measure thickness. A Rame-Hart 100 Goniometer was used to measure water contact angle.

## Materials and Methods

**Materials.** The basic film compositions are shown in Table 1 and properties are shown in Table 2.  
**Sol-Gel synthesis.** Using two methods described in the literature,<sup>2,3</sup> ormosil films containing silanes 1-6 or dodecyl pyridinium chloride were synthesized (Table 1).  
**Imprinting.** DNT (0.02 M-1.0 M) was stirred with sol-gel E for 1 h. Use of surfactant (dodecylpyridinium chloride) resulted in an unstable film.  
**Film formation.** Sol-gels were spin-coated onto Si (2" wafers cut into quarters, Wafer World) or fused silica substrates (1"x1" Dell Optics) cleaned using the RCA acid cleaning method. Aliquots of 40 μL were spun at 4000 rpm for 40 s; the films were air-dried for 24-48 h and stored in a laminar flow hood.  
**Template removal.** Two methods were used to remove the templates sonication and Soxhlet extraction. DNT was partially removed from films using sonication in methanol, methylene chloride, and methanol for 10 min each. Soxhlet extraction was carried out in methanol for 24 h.  
**Vapor exposure.** Films were exposed to DNT vapor at room temperature in tightly sealed Teflon jars.  
**UV Characterization.** UV absorbance was measured using an Agilent Technologies Diode Array Spectrophotometer. Unimprinted films were used as background spectra.

## Spectroscopic Characterization

**UV Spectroscopy.** Films made with organosilanes 5 and 1 (Film E), templated with 0.02 M DNT, were extracted, then exposed to DNT vapor (Figure 8).

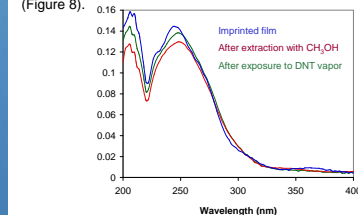


Figure 8. UV spectra for ormosil film imprinted with DNT (blue line), after Soxhlet extraction with methanol (red line), and after exposure to DNT vapor (green line).

## Conclusions

- Calculated angular mode shifts in organosiloxane model films for refractive index changes of 0.01% to 1% ranged from 0.1° to 1.5°. This is a detectable range for the portable flow cell sensor.
- Ormosil films containing phenyl, amino, methyl amino, epoxy, and methyl substituents were synthesized with thicknesses ranging from 600 to 800 nm.
- Most films appear smooth and transparent.
- DNT was incorporated into films and could be removed by solvent extraction.
- Surfactant-containing films were completely removed during template extraction.
- Exposure of templated films to DNT vapor resulted in increased DNT.

## References

- Sanchez, C.; Boissiere, C.; Grosso, D.; Laberty, C.; Nicole, L. *Chem. Mater.* **2008**, *20*, 682-737.
- Fireman-Shoresh, S.; Avnir, D.; Marx, S. General Method for Chiral Imprinting of Sol-Gel Thin Films Exhibiting Enantioselectivity. *Chem. Mater.* **2003**, *15*, 3607-3613.
- Fireman-Shoresh, S.; Popov, I.; Avnir, D.; Marx, S. Enantioselective, Chirally Templated Sol-Gel Thin Films. *J. Am. Chem. Soc.* **2005**, *127*, 2650-2655.
- Robertson, W. M.; Arjavalingam, G.; Meade, R. D.; Brommer, K. D.; Rappe, A. M.; Joannopoulos. Observation of Surface Photons on Periodic Dielectric Arrays. *Opt. Lett.* **1993**, *18*, 528-530.
- Woodfin, R. L., ed. *Trace Chemical Sensing of Explosives*, Wiley: New Jersey, 2007; Senesac, L.; Thundat, T. G. Nanosensors for trace explosive detection. *Materials Today*, **2008**, *11*(3), 28-36.

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