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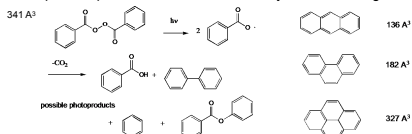
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Introduction

Imprinted materials have broad applications including sensors, enantioselective materials, filters, and catalysts.¹ Organically-modified silicate (ormosil) films are hybrid materials resulting from sol-gel processing of orthosilicates and mixtures of organosilanes. In this project, two types of imprinted ormosil films^{2,3} were designed to recognize 1) explosives vapors and 2) polycyclic aromatic hydrocarbons (PAHs).

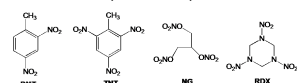
Film Design. The organic materials in the ormosil films were chosen to mimic the polarity and size of the analytes.

Self-destructive templates. In one film design, benzoyl peroxide was used as a thermally labile template with similar size and polarity to PAHs. Scheme 1 illustrates expected thermal and photochemical decomposition products that could allow easy removal of fragments.



Scheme 1. Expected products of thermal or photochemistry and possible PAH analytes. Molecular volumes for BP and each proposed PAH analyte are shown near each structure and were calculated with HF 321 G*.

Vapor Sensors. In a second design, 2,4-dinitrotoluene (DNT) was used as a template with similar size and polarity to 2,4,6-trinitrotoluene (TNT). These and other common explosives are pictured below.



Sensing at PBGM Surfaces

Ultimately, the sensor platform used to detect analytes entrapped in films will be a multilayered photonic band gap material (PBGM). Figure 1 shows the sample configuration. The PBGM, a multilayered SiO₂/TiO₂ film, creates surface optical waves that propagate at the air/surface interface when light is incident at an appropriate angle. This evanescent field couples to surface plasmons (SP), resulting in a reduction in the reflected light. The reflectivity dip as a function of incident angle illustrates the high sensitivity of PBGM to the angular position of the dip relative to metals (Figure 2).⁴

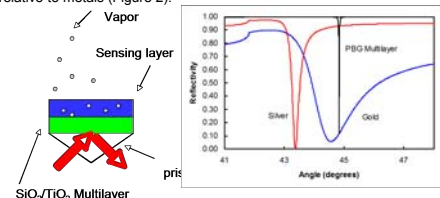
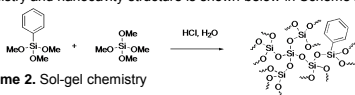


Figure 1. Nanoporous ormosil films on PBGM exposed to vapor during analysis

Figure 2. Reflectivity dip of metals vs. PBGM

Materials and Methods

Materials. The basic film syntheses are shown in Table 1 and properties are shown in Table 2. An idealized Scheme of sol-gel chemistry and nanocavity structure is shown below in Scheme 2.



Scheme 2. Sol-gel chemistry

Sol-Gel synthesis. Using two methods described in the literature,^{2,3} ormosil films containing silanes 1-6 or surfactant dodecyl pyridinium chloride were synthesized using conditions in Table 1.

Imprinting. Templates were stirred in the sol-gel for 1-2 h. BP was included at 0.01-0.04 M. DNT was doped from 0.02 - 1.0 M. **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 decomposition. BP templates were heated at 100 °C or irradiated with a 450 W med pressure for 1 - 30 min.

Template extraction. Two methods were used to remove the DNT template and photo- or thermal decomposition products from BP: sonication and Soxhlet extraction. DNT was partially removed from films using sonication in methanol, methylene chloride, and methanol for 10 minutes each. Soxhlet extraction in methanol for 24 h removed only 10% of the DNT (Figure 2).

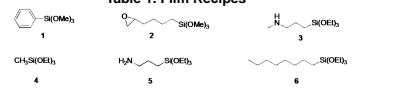
Exposure to PAH analytes. BP-imprinted films were exposed to solutions of 10⁻⁵ M - 10⁻³ M anthracene, phenanthrene, or pyrene in methanol or methylene chloride. No UV absorbances or fluorescence due to these PAHs were observed.

DNT vapor exposure. Films from which DNT was extracted were exposed to DNT vapor in tightly sealed Teflon jars at room temp.

UV Characterization. UV absorbance was measured using Diode Array Spectrophotometer. Unimprinted films were used for background spectra.

Film Synthesis

Table 1. Film Recipes



Recipe ^a	TMOS	TEOS	PTMOS	Silane (#)	HCl	Water	Ethanol	Time (h)
A	2.00	-	0.50	1	0.66 ^b	0.66	2.00 ^c	2
B	3.00	-	0.20	2	1.00 ^b	1.00	5.87	2
C	-	3.00	0.20	3	0.10	1.00	3.00	2-5
D	-	3.00	0.20	6	0.10	1.00	3.00	5
E	-	3.00	0.20	5	0.10	1.00	3.00	2-24
F	3.00	-	0.37	4	1.00 ^b	1.00	3.00	2
G	1.1	-	0.34	7 ^d	0.8 ^b	0.5	2.2 ^e	3.5

^aAll reagents in mL; ^b0.1M HCl; ^cethoxyethanol; ^d1-dodecylpyridinium chloride hydrate; ^e1-butanol.

Film Properties

Table 2. Film Thickness and Contact Angles

Film	Thickness (Ellipsometric, nm)	Thickness (Profilometric, nm)	Water Contact Angle θ (adv/ret)
E	767 ± 1	775 ± 1	68 ± 2 / 64 ± 1
A	651 ± 4	711 ± 1	66 ± 2 / 64 ± 1
A	749 ± 11	774 ± 1	62 ± 1 / 61 ± 2
B	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.

Template Decomposition

UV Spectroscopy. BP film. UV of films on fused silica was used to quantify the amount of template and phenyl groups within the films. Figure 2 shows film A containing BP. The inset illustrates the disappearance of BP upon heating and the resulting $t_{1/2} = 1$ hour at 100 °C. Irradiation with 254 nm light increased the rate of BP disappearance, as did heating in films with polar groups (recipe E).

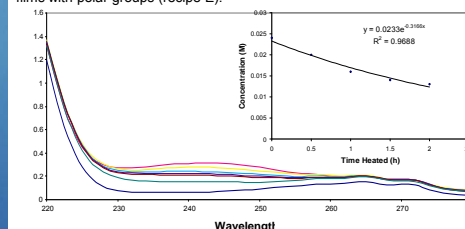


Figure 2. UV spectra showing the decomposition of BP within Film A. The inset shows the decrease in absorbance at BP λ_{max} as the film was heated at 100 °C.

Calibration Curves. The calibration curve of benzoyl peroxide was created by preparing known concentrations of benzoyl peroxide in sol-gel recipe C. Fluorescence calibration curves of the PAHs allow us to estimate the amount of the PAH incorporated into the nanocavities.

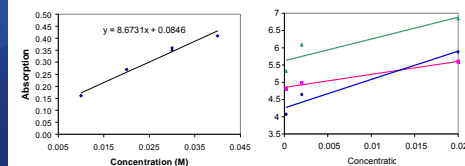


Figure 3. Calibration curve for UV absorption vs concentration of BP. Figure 4. Calibration curves for PAHs - fluorescence intensity vs. concentration

UV Spectroscopy

UV Spectroscopy of DNT films. Films made with organosilanes 5 and 1 (recipe E) and imprinted with 0.02 M DNT were extracted with methanol in a Soxhlet extractor for 24 hours and exposed to DNT vapors.

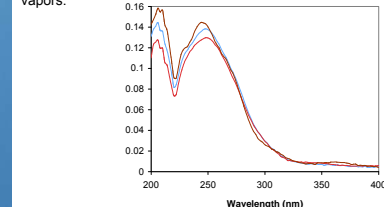


Figure 8. UV spectra for ormosil film imprinted with DNT (brown line), after Soxhlet extraction with methanol (red line), and after exposure to DNT vapor (blue line).

Conclusions

- Ormosil films containing phenyl, amino, methyl amino, epoxy, and methyl substituents were synthesized with thicknesses ranging from 600 to 800 nm.
- Benzoyl peroxide was doped from 0.04-0.01 M.
- Most films appear smooth and transparent.
- Thermal decomposition of benzoyl peroxide within the phenyl substituted film was first order kinetics with $t_{1/2} = 1$ h at 100 °C
- Films with BP templates did not recognize PAHs within the limit of sensitivity of UV and fluorescence detection.
- DNT was incorporated into films containing 5 and 1. In these amine-containing films, sonication or Soxhlet extraction removed only small amounts of DNT.
- Films containing surfactants were removed from substrates during extraction.
- Calcification of films containing DNT resulted in no change, with the exception of films older than one month, which crystallized.
- Exposure of templated films to DNT vapor resulted in increased DNT in the films.

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Acknowledgements

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