

# Pore-Bridging Poly(dimethylsiloxane) Membranes as Selective Interfaces for Vapor-Phase Chemical Sensing

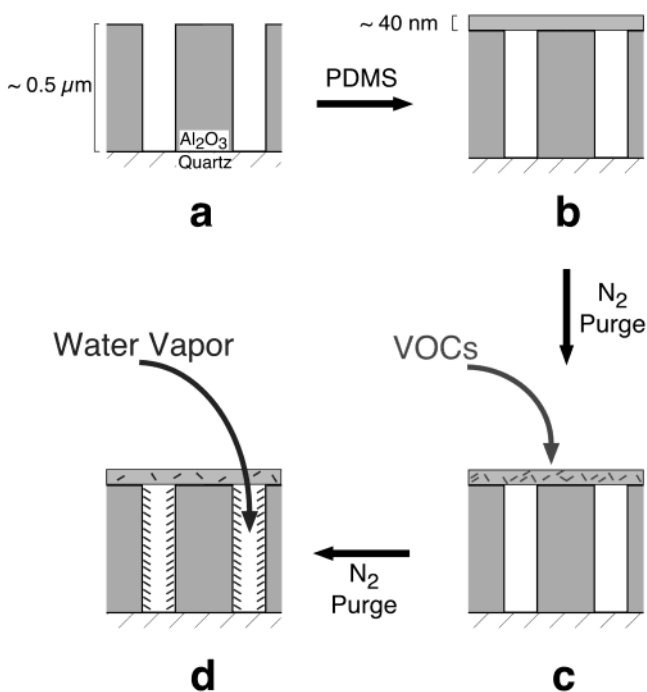
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A new kind of polymer-based sensor is described in which the experimental parameters controlling selectivity and sensitivity are decoupled. The sensor is based on a surface acoustic wave (SAW) gravimetric transducer modified with a high-surface-area, nanoporous alumina coating. A very thin ( $\sim 40$  nm) poly(dimethylsiloxane) (PDMS) coating resides atop the porous alumina structure. In this configuration, the total surface area of the nanoporous alumina coating controls the sensitivity of the device, while the chemical properties of the PDMS membrane control selectivity. In conventional polymer-based sensors, the polymer plays the dual role of controlling both selectivity (via the chemical composition of the coating) and sensitivity (via the volume of the film). In this paper, we show that PDMS acts as a chemically selective gate that absorbs polar and nonpolar VOCs but does not transport these analytes to the underlying pore volume. In contrast, water vapor is absorbed by the PDMS to a very minor extent but is easily transported through it to the underlying walls of the porous substructure. Specifically, there was little difference in the mass-loading response arising from polar and nonpolar VOCs dosed onto planar and nanoporous SAW devices modified with PDMS. In contrast, SAW devices having nanoporous coatings responded up to 24 times more selectively to water than planar sensors modified identically.

We report a new type of chemically selective gravimetric vapor sensor, which is based on a polymeric coating that controls access to underlying pores. Because the pores have a very high surface area, significant signal enhancement is observed only for analytes that are able to penetrate the membrane and adsorb to the surface of the underlying pores (Scheme 1). The sensor consists of three parts: a surface acoustic wave (SAW) transducer, a porous alumina coating, and a thin, spin-cast polymeric layer. Frames c and d of Scheme 1 show how the sensor functions: volatile organic compounds (VOCs) sorb into the polymeric coating but do not access the underlying anodically etched nanoporous (NP) alumina substrate. In contrast, water vapor sorbs into the polymer to a small extent, but it also permeates through the polymer to adsorb onto the accessible surface area of the pores. Thus, the poly-(dimethylsiloxane) (PDMS) membrane is a selective gate that is

Scheme 1



open for water and shut for organic compounds. Additionally, the extent of VOC sorption into the PDMS membrane depends on the specific identity of the VOC, and therefore, this sensor is also selective for VOCs but with lower sensitivity. In this paper, we report a refined method for fabricating the nanoporous alumina coatings, the deposition of the polymer film, and quantitative gravimetric sensing results.

We previously showed that composite polymer films having a thickness on the order of 10 nm can act as nonselective gates that either admit or exclude VOCs from pores residing beneath the polymer film.<sup>1</sup> For example, deposition of a monolayer of generation six, amine-terminated poly(amidoamine) (PAMAM) dendrimers<sup>2,3</sup> atop a NP alumina SAW device resulted in a 17% attenuation in *n*-heptane permeability. However, following modification with poly(maleic anhydride)-*c*-poly(methyl vinyl ether) (Gantrez), a factor of 4 decrease in permeability was observed.

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Finally, upon cross-linking with additional PAMAM dendrimers, the resulting 12-nm composite film was nearly impermeable to the analytes present in the VOC test set. Although these polymeric gates were able to modulate analyte permeability, they did not impart selectivity.

To address the issue of chemical selectivity we have chosen to study PDMS (SE-30GC) as a pore-bridging coating. PDMS is a rubbery-solid material that has been extensively used for applications related to gas chromatography and solid-phase microextraction (SPME).<sup>4–6</sup> PDMS films have been deposited onto sensing platforms by spray-coating,<sup>7–10</sup> solution-casting,<sup>11</sup> and spin-coating.<sup>12–14</sup> The thickness of these films is as small as 40 nm. Chemical sensors based on PDMS coatings atop thickness shear mode (TSM) and SAW resonators,<sup>8,10,11,15</sup> and even atomic force cantilevers,<sup>16</sup> have also been described.

Two recent findings are particularly important to the formulation of the present study. First, it has been found that nonpolar analytes preferentially partition out of water and into PDMS-coated SPME fibers.<sup>4–6</sup> Second, Hierlemann and co-workers investigated the partition coefficients of a variety of VOCs in “acoustically thin”<sup>17</sup> coatings of PDMS and other polysiloxanes using TSM oscillators.<sup>10</sup> Their results indicate that the PDMS partition coefficients for nonpolar analytes are higher than for polar analytes.

Here, we describe the selectivity properties of chemical sensors fabricated from SAW transducers and PDMS films spin-cast atop nanoporous alumina membranes. The mass-loading response for the following analytes, which represent a broad spectrum of chemical classes, were evaluated: acetonitrile, ethanol, benzene, heptane, and water vapor. Although the thickness of the PDMS film is only ~40 nm, the data show that the VOC analytes preferentially sorb into the polymer, but they do not transverse it to a significant extent. In contrast, water vapor easily penetrates the film and adsorbs to the surface of the underlying nanopores. In this way, the PDMS overlayer functions as a selective gate that controls access of vapor-phase analytes to the enhanced surface area represented by the nanopore walls.

## EXPERIMENTAL SECTION

**Chemicals.** The following chemicals were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and used as received: benzene (99.5%), *n*-heptane (99+%), dichloromethane (99.8%), and acetonitrile (99.8%). Sulfuric acid, concentrated (EM Science, Gibbstown, NJ), was used as received. Pure ethanol (100%, Aaper Alcohol and Chemical Co., Shelbyville, KY) was used as received. All water was purified to a resistivity of 18 MΩ·cm using a Milli-Q reagent water system (Millipore, Bedford, MA). Poly(dimethylsiloxane) (SE-30, methyl silicone) (Supelco, Bellefonte, PA) was used as received and dissolved in dichloromethane prior to use. N<sub>2</sub> gas used for mass measurements and Fourier transform infrared-external reflectance spectroscopy (FT-IR-ERS) was obtained from liquid N<sub>2</sub> boil-off and passed through a Drierite gas-drying unit (Hammond 26800, Fisher Scientific Co., Pittsburgh, PA) before use.

**Substrates.** The procedure for preparing the NP alumina coatings on quartz SAW devices was adapted from a previously reported protocol.<sup>1,18</sup> Complete details are provided in the Supporting Information, but a brief summary is provided here. First, 500 nm of Al metal was evaporated onto a quartz SAW device maintained at 250 °C. The elevated temperature promotes formation of columnar grain structures.<sup>18</sup> Second, the Al coatings were anodized in a three-electrode cell to yield NP alumina. This was accomplished by making electrical contact to the Al substrate at a single point with a sharpened titanium spring clip. The counter electrode was Pt gauze, and it was positioned parallel to the Al substrate at a distance of 2 cm. A mercury/mercurous sulfate reference electrode (CH Instruments, Inc., Austin, TX) was positioned off-center and equidistant between the other two electrodes. The potential of the working electrode was maintained using a model CHI660A electrochemical workstation (CH Instruments, Inc.). Anodization was performed under quiescent conditions in a freshly prepared aqueous sulfuric acid solution (10% w/v). The Al anodization was carried out at a potential of 2.5 V (vs Hg/Hg<sub>2</sub>SO<sub>4</sub>), and the current was monitored throughout the experiment. The anodization current gradually decayed as the available Al was converted to nanoporous alumina.<sup>18</sup> As the anodization proceeds, the current eventually reaches a steady-state value indicating that Al conversion is complete. Additional anodization beyond this point results in horizontal expansion of the pores. Following anodization, the substrate was removed from the electrolyte solution, rinsed thoroughly with purified water, dried under a N<sub>2</sub> gas stream, and then stored until needed in a N<sub>2</sub>-purged desiccant box.

Nonporous Al substrates were prepared on Si(100) substrates using conditions identical to those described in the previous paragraph for NP-coated SAW devices. These substrates were diced into 2.6 cm × 1.3 cm pieces and used for ellipsometric measurements and FT-IR-ERS spectroscopy because the NP alumina surfaces were insufficiently reflective for this purpose. Some gravimetric experiments were also carried out using SAW devices coated with Al but not anodized. These are referred to in the text as planar Al substrates and planar Al SAW devices, respectively.

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**Chemical Modification of Substrates.** All SAW devices (planar and NP) and Al-coated Si wafers were initially cleaned in a low-energy ozone cleaner for 15 min (model 135500, Boekel Industries, Inc.). The substrates were then sonicated for 2 min in ethanol, rinsed with ethanol for 1–2 min, dried under a stream of N<sub>2</sub> gas, and then dried under vacuum for 0.5 h at 25 °C. Subsequently, PDMS (10 mg/mL in CH<sub>2</sub>Cl<sub>2</sub>) was spin-cast onto the SAW devices and the Si wafers for 30 s at 3000 rpm, with 1-s acceleration and deceleration ramp times, and an initial 25-s stationary delay time using a model P6204 spin coater (SCS Cookson, Indianapolis, IN). Upon completion of the spin-coating process, these PDMS-modified substrates were analyzed using methods described later.

**Mass Measurements.** Mass measurements were made in parallel at 21 ± 1 °C using two ST-cut quartz oscillators housed in a custom-built flow system.<sup>1,19,20</sup> SAW devices were dosed with vapor-phase probe molecules nominally present at 10% of saturation ( $p/p_{\text{sat}}$ ) in a flowing N<sub>2</sub> stream (flow rate, 0.5 L/min). Additional experimental details are provided in the Supporting Information. The relative volatility of the VOCs increases in the order heptane, ethanol, acetonitrile, and benzene.<sup>21</sup>

**Ellipsometric Thickness Measurements.** Ellipsometric thickness measurements were obtained before and after spin-coating the PDMS films using a Gaertner Scientific (Chicago, IL) model L2W26D ellipsometer.<sup>22</sup> Additional experimental details are provided in the Supporting Information.

**Fourier Transform Infrared-External Reflection Spectroscopy.** FT-IR-ERS measurements were obtained from modified Al-coated Si wafers using a Bio-Rad FTS-6000 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid N<sub>2</sub>-cooled mercury cadmium telluride detector.<sup>22</sup> Low surface reflectivity precluded direct measurement of IR spectra on the NP alumina substrates, and thus, we postulate that the surface IR spectra of PDMS on the NP and planar alumina substrates are the same. Additional experimental details are provided in the Supporting Information.

**X-ray Photoelectron Spectroscopy (XPS).** XPS spectra were obtained from PDMS-coated NP alumina SAW devices using an Axis HSi 165 Ultra Kratos spectrometer (Kratos, Manchester, MA). Additional experimental details are provided in the Supporting Information.

**Field Emission Scanning Electron Microscopy (FE-SEM).** FE-SEM imaging was performed using a Hitachi S4500 scanning electron microscope (Tokyo, Japan) outfitted with a field emitter gun. To minimize charging, a low acceleration voltage was utilized (5 kV; emission current, 20 μA). Digital images were acquired with Princeton Gamma Tech hardware in conjunction with Imix software (PGT, Rocky Hill, NJ). The samples were Cr-coated using a Gatan, model 681 high-resolution, ion beam coater (Pleasanton, CA) to a nominal thickness of 1.9 nm.

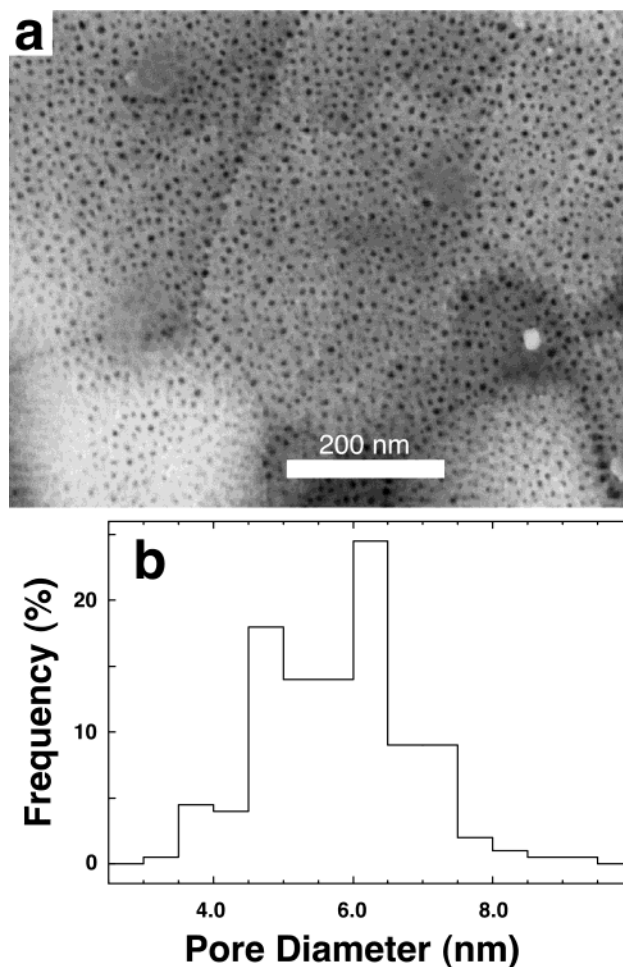


Figure 1. (a) Top-view FE-SEM micrograph of a naked nanoporous alumina SAW substrate. (b) Histogram illustrating the distribution of pore diameters.

## RESULTS AND DISCUSSION

The NP alumina coatings used in this study were prepared using a modification of a previously described method.<sup>18</sup> These improvements have led to a decrease in the pore diameter and improvement in the monodispersity of the pore size. Complete details of the new methodology are available in the Experimental Section and the Supporting Information. Figure 1a shows a representative FE-SEM of a NP alumina substrate. The average pore diameter is  $5.8 \pm 3.5$  nm (Figure 1b), which can be compared to our previous result of  $6.8 \pm 4.8$  nm.<sup>1</sup> The pore number density, averaged over five different  $0.1 \mu\text{m} \times 0.1 \mu\text{m}$  regions, is  $(4.1 \pm 0.2) \times 10^3$  pores/ $\mu\text{m}^2$ , which is comparable to our previous values of  $(3.8 \pm 0.5) \times 10^3$  pores/ $\mu\text{m}^2$ .

It is possible to roughly estimate the true surface area of these coatings based on the pore number density, the average pore diameter, and the thickness of the NP alumina coating ( $0.60 \pm 0.01 \mu\text{m}$ ). This calculation results in a roughness factor (true area/projected area) of 38, assuming discrete, cylindrical pores. This can be compared to a measured roughness factor of 37 determined by measuring the mass of *n*-heptane that adsorbs to a naked NP alumina substrate.<sup>1</sup>

Because of the porosity of these NP alumina films, there is insufficient substrate reflectivity to directly characterize the

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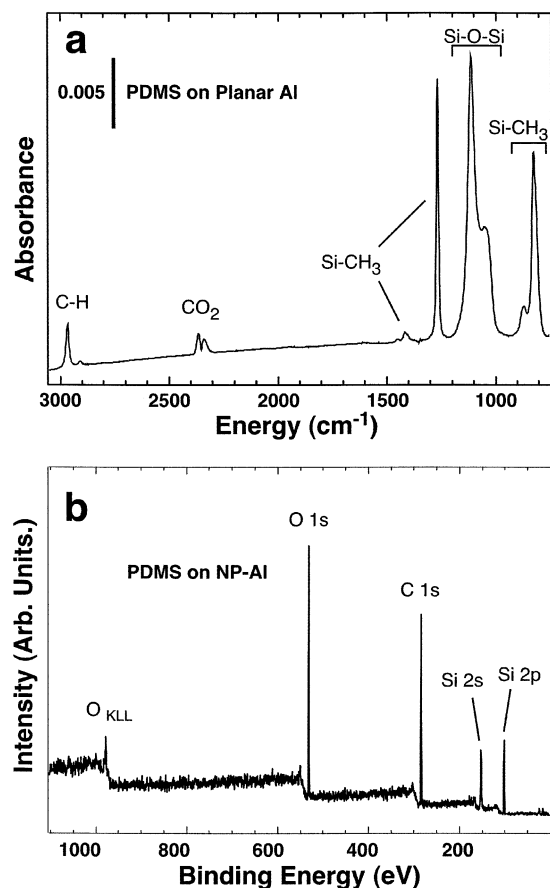


Figure 2. (a) FT-IR-ERS spectrum of a PDMS coating atop a planar Al substrate. (b) XPS spectrum of a PDMS coating atop a NP alumina substrate (frame b, Scheme 1).

polymer overlayers by ellipsometry or FT-IR-ERS. Accordingly, Al was evaporated onto Si substrates using exactly the same deposition conditions used to prepare the NP alumina substrates, and these planar Al substrates were characterized spectroscopically. Although the surface properties of the planar Al and NP alumina are not identical, the thin native oxide layer on the planar substrate should be quite similar to the NP alumina coating. Figure 2a shows an FT-IR-ERS spectrum of a planar Al substrate after modification with a spin-cast PDMS film having a measured ellipsometric thickness of 40 nm. The spectrum shows characteristic siloxane (Si-O-Si) stretching bands at 1111 and 1049 cm<sup>-1</sup>,<sup>23</sup> confirming the presence of the PDMS film on the surface. Additionally, the Si-CH<sub>3</sub> groups give rise to the asymmetric and symmetric stretching peaks at 1412 and 1265 cm<sup>-1</sup>, respectively, as well as the CH<sub>3</sub> rocking band at ~850 cm<sup>-1</sup>.<sup>23</sup>

XPS was used to confirm that PDMS conformally coats the NP alumina surface. Figure 2b shows an XPS spectrum obtained from a PDMS-coated NP alumina-coated SAW device. Prominent peaks are observed for Si, O, and C, indicating the presence of PDMS. However, there is no evidence of the Al 2s or Al 2p peaks, which would be present at approximately 118 and 73 eV, respectively. This means the NP alumina coating is fully masked by the ultrathin polymer overlayer.

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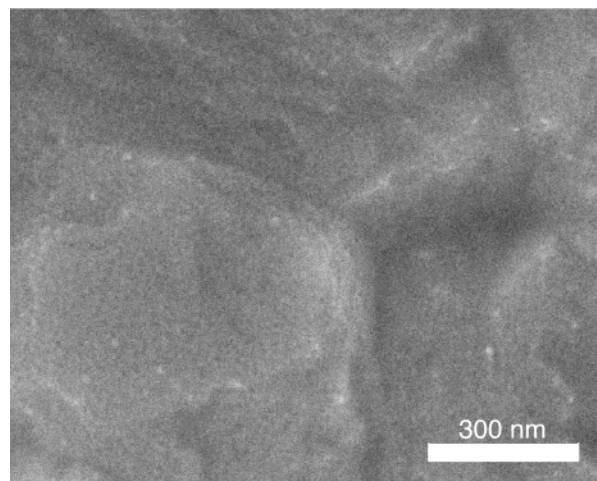


Figure 3. Top-view FE-SEM image of a SAW device modified with a NP alumina coating and subsequently with ~40 nm of PDMS (frame b, Scheme 1). The image reveals a conformal polymer coating and no evidence for agglomeration of the polymer.

The FE-SEM micrograph shown in Figure 3 was obtained from an NP alumina-coated SAW device after addition of a spin-cast PDMS film. The pores in the NP alumina substrate remain visible through the polymer film, and there is no indication of polymer agglomeration. Taken together, the ellipsometry, FT-IR-ERS, XPS, and FE-SEM data strongly suggest that the NP alumina SAW device films are conformally coated with a ~40-nm-thick layer of PDMS.

Parts a and b of Figure 4 show gravimetric response data for PDMS-modified planar Al and NP alumina SAW devices in the presence of the five vapor-phase analytes used in this study. Pairs of SAW devices having nominally identical PDMS overlayers (estimated thickness, 38 nm) were simultaneously dosed with VOCs present at 10% of saturation ( $p/p_{\text{sat}}$ ) in a N<sub>2</sub> carrier gas. The data are displayed as the frequency shift ( $\Delta f$ ) versus time. The dosing experiment begins with a 5-min N<sub>2</sub> purge to establish a baseline. Next, the pair of SAW devices was simultaneously dosed with acetonitrile, ethanol (EtOH), benzene (Benz), *n*-heptane (C7), water vapor, and then acetonitrile again. Each analyte was dosed twice in series for 60 s, and after each exposure to a VOC, the system was purged with pure N<sub>2</sub> for 180 s. The dosing experiments were performed on two independently prepared pairs of SAW devices. SAW devices coated with the same thickness of PDMS exhibited responses within 10% of each other.

The dosing experiment illustrates that the gravimetric response for acetonitrile on the PDMS-modified NP alumina SAW device is nearly identical to the response observed on the similarly modified planar Al SAW device. That is, the entire mass loading response, in the presence or absence of the underlying pores, arises exclusively from absorption of acetonitrile into the PDMS membrane. This means that the underlying porosity of the NP alumina is not accessible to the acetonitrile vapor, and this in turn means that the PDMS overlayer acts as a closed gate for this VOC. Control experiments discussed later indicate that the mass of acetonitrile that sorbs to a PDMS-free NP alumina SAW device is ~40 times higher than for the PDMS-modified sensor. The behavior of the other VOCs is very similar to acetonitrile: in all cases, the mass loadings of PDMS-coated planar Al and NP alumina SAW devices are within 5% of one another. Additionally,

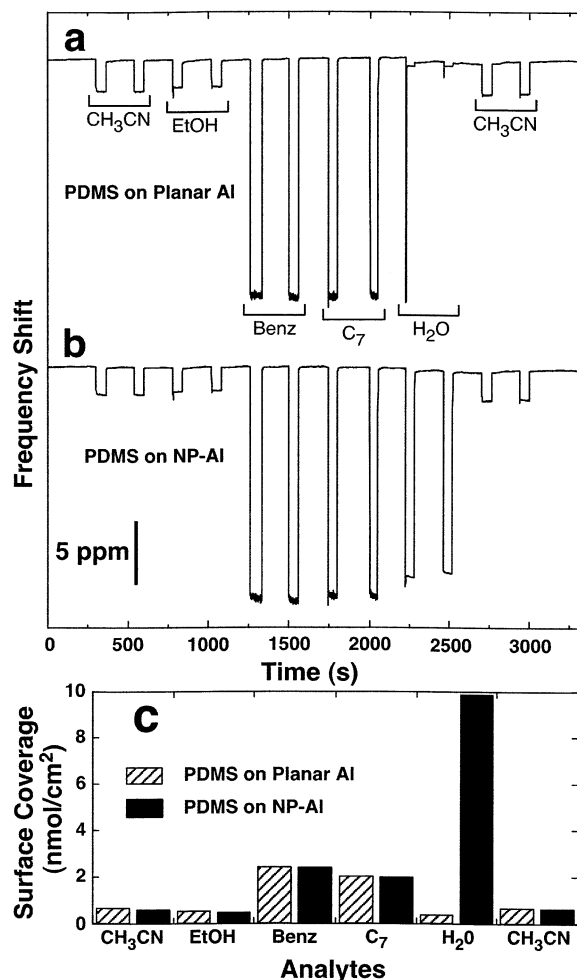


Figure 4. Mass-loading profiles for SAW devices modified with a thin layer of PDMS atop (a) planar Al and (b) NP alumina coatings. The SAW devices were dosed with 10%-of-saturation acetonitrile, ethanol, benzene, heptane, water, and again with acetonitrile. The large apparent-mass response observed for the first water-dosing measurement in (a) is a consequence of a pressure transient associated with the actuation of the analyte dosing valve. (c) A histogram, derived from frames a and b showing surface coverage of the analytes on the PDMS-modified planar and NP alumina SAW devices in units of surface concentration, which removes the molecular weight bias of the analytes.

as previously shown by Hierlemann and co-workers, PDMS exhibits enhanced mass loading for the two nonpolar VOCs (benzene, *n*-heptane) compared to the more polar acetonitrile and ethanol dosants.<sup>10</sup>

In contrast to the VOCs, the behavior observed for water is reversed. Specifically, water is poorly absorbed by the PDMS coating, but it easily penetrates through it and sorbs to the underlying surface of the nanopores. Figure 4c compares the mass-loading response of the five analytes in terms of surface concentration (nmol/cm<sup>2</sup>, which cm<sup>2</sup> refers to the projected surface area), which removes the molecular weight bias from the raw frequency shift data. These data show that the PDMS-coated planar Al and NP alumina surfaces yield comparable loading values for the VOCs. However, the water vapor response is 24 times larger for the NP surface compared to the planar surface, indicating that water is able to permeate through the PDMS coating and encounter the surface of the underlying pores. Note

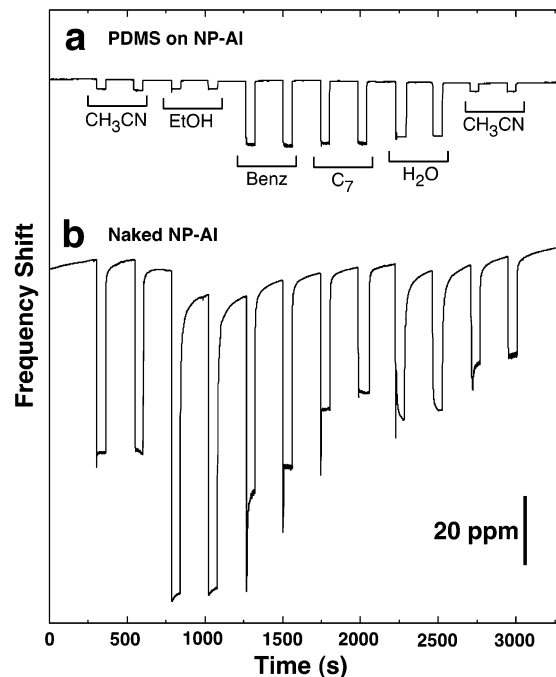


Figure 5. Mass-loading profiles of nominally identical NP alumina-modified SAW devices. In (a), the surface was modified with PDMS, and in (b), no PDMS membrane was present. The SAW devices were dosed with 10% of saturation acetonitrile, ethanol, benzene, heptane, water, and again with acetonitrile.

that thicker PDMS membranes (>80 nm) do not exhibit this enhanced selectivity for water.

We performed control experiments to confirm that the PDMS coating is responsible for introducing selectivity to the SAW-based sensor. Specifically, Figure 5 compares the mass-loading response of a PDMS-modified NP alumina SAW device with an identically prepared SAW device not coated with PDMS. The data in Figure 5a, which were obtained from a PDMS-coated NP alumina-coated SAW device, replicate the results shown in Figure 4b; in fact, in all such duplicate experiments we performed, the device-to-device responses were within 16% of one other. The important point, however, is that adsorption of the VOCs onto the entire exposed alumina surface is not hindered by the pore structure (Figure 5b). For example, the mass loading of acetonitrile in the absence of the PDMS membrane is 26 times higher than when the membrane is present. Note also that the PDMS-free SAW sensor does not select for VOCs based on their hydrophobicity. This set of experiments demonstrates that the ultrathin PDMS membrane is responsible for nearly eliminating VOC adsorption onto the walls of the underlying porous substructure of the NP alumina.

The data in Figure 5 also indicate that the PDMS thin film reduces the maximum extent of water vapor sorption compared to the PDMS-free NP alumina substrate. Specifically, the water vapor response is 2–3 times greater on the naked NP substrate compared to the PDMS-modified NP SAW device. This means that the selective PDMS coating reduces the sensitivity of the device by a factor of 2–3. This is probably a consequence of partial passivation of the alumina surface with PDMS.

## SUMMARY AND CONCLUSIONS

In this paper, we have shown that access of vapor-phase analytes to the intrinsically high surface area walls of nanoporous

substrates can be selectively gated in the presence of an ultrathin PDMS membrane. Our approach is in contradistinction to the usual method for constructing polymer-based sensors, which involves deposition of a chemically sensitive polymer thin film onto a passive planar surface. In such devices, the polymer plays the dual role of controlling both selectivity (via the chemical composition of the coating) and sensitivity (via the volume of the film). The unique aspect of our new strategy is that the selective coating only serves to control selectivity by mediating transport of the analyte to the underlying alumina surface area. The underlying porous structure independently controls sensitivity. Clearly, thinner, conformal membranes would be expected to perform this function even more efficiently.

#### ACKNOWLEDGMENT

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#### SUPPORTING INFORMATION AVAILABLE

Detailed experimental information regarding materials fabrication and substrate characterization by gravimetry, ellipsometry, X-ray photoelectron spectroscopy, and infrared spectroscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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