

Supplementary Information

Towards universal enrichment coating for IR-ATR waveguides

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S1. Experimental

Materials

Poly(glycidyl methacrylate), PGMA was synthesized according to a previously published¹ procedure and had Mn= 135 kDa and PDI= 2.97 measured by GPC (Waters Breeze). Polyacrylic acid, PAA was purchased from Sigma Aldrich (Mn=100 kDa). Polybutadiene was purchased from Sigma Aldrich (Mn= 471 kDa) and epoxidized up to 60 mol% as described elsewhere² to give epoxidized polybutadiene (EPB). Carboxy terminated poly 2-vinylpyridine, P2VP was purchased from Polymer Source (Mn= 53 kDa). Silicon crystal waveguides used in the infrared experiments were purchased from Harrick and were 45° trapezoids. Sulfuric acid and hydrogen peroxide were purchased from Sigma Aldrich and LabChem Inc., respectively and mixed at a 3:1 ratio to make “piranha” solution. Vapor cells for ellipsometry and infrared spectrometry were made from glass and machined on site. Kalrez o-rings, used to seal the perimeter of the infrared cell, were purchased from McMaster-Carr. Analytes tested included methanol, ethanol, isopropanol, acetone, acetic acid, hexane, and 0.1% ammonium hydroxide were purchased from Sigma Aldrich.

Fabrication of ChG micro-disc resonators

Bulk Ge₂₃Sb₇S₇₀ glass for film deposition was prepared from high purity elements using a traditional melt-quenching technique. The synthesis procedures of the bulk As- and Ge-based glasses used in this study are explained in detail, elsewhere.^{3, 4} All glasses are prepared from high purity elements (As, Alfa Aesar 99.999%; Ge, Alfa Aesar 99.999%; Sb, Sigma Aldrich 99.9%; S, Sigma Aldrich 99.999%) with no further purification. Thus starting bulk glasses used for target materials for film deposition have measurable loss in the near and mid-infrared region of the spectrum due to quantities of adsorbed oxide and hydride. Ge₂₃Sb₇S₇₀ glass films are thermally deposited from targets of bulk glass pieces onto substrates in an Edwards E306A single-source evaporator using an optimized procedure described elsewhere.⁵ The substrates for thin film deposition were 6 inch Si wafers pre-coated with a 3µm-thick thermal oxide (Silicon Quest International Inc.). Waveguides and micro-disc resonators were fabricated by a lift-off process: reverse photoresist patterns of the device were formed on the substrates prior to chalcogenide glass deposition. Details of the lithographic device fabrication can be found elsewhere.⁶

Synthesis of polymer multilayered coating

Silicon wafers and crystals were cleaned by sonication in DI water followed by sonication in piranha solution in a warmed water bath for 2 hours minimum for wafers and 4-5 hours for crystals. The wafers and crystals were thoroughly rinsed with DI water after the piranha solution treatment. To obtain the multilayered coating polymer layers were anchored via the “grafting to” approach.² Prior to the grafting a polymer layer was deposited on the surface (of silicon crystals and silicon wafers) by dip coating (Mayer Fientechnik D-3400 at 240mm/min). Polymer solutions for dip coating were prepared with concentrations of 0.07% w/v PGMA, 1% w/v PAA, 0.5% w/v EPB, and 0.5% w/v P2VP. Chloroform was used as the solvent for all polymers

except PAA for which methanol was used. The general procedure for dip coating and grafting is described elsewhere.^{7, 8} Conditions of grafting for PGMA, PAA and EPB layers were 120°C for 20 minutes while P2VP was grafted at 150°C over 15 hours. After annealing the samples were rinsed 4 times with a solvent to remove any ungrafted polymer. The same procedure was used for grafting of the polymers to the micro-disc resonators. The resonators were rinsed with MEK prior to the grafting instead of the piranha solution. Thicknesses of the polymer layers, determined by ellipsometry with $\pm 5\%$ error, were: PGMA = 2 nm, PAA and EPB = 8 nm, PGMA=7 nm, and P2VP= 2 nm. Beside the P2VP layer, these thickness values represent the highest amount which can be grafted at the conditions used. The thicknesses are typically reproducible with accuracy of ± 1 nm. For the P2VP layer higher deviation in thickness was experimentally observed. In some experiments up to 7 nm of P2VP could be grafted.

Ellipsometry

The ellipsometer used was from InOm Tech Products Inc. model COMPEL ELC-11. The refractive index of each polymer was assumed to be 1.5. Swelling analysis was conducted by placing the wafer covered with the multilayered coating in a closed cell with a bucket of analyte. The swelling curves presented in **Figure S1** are the average of three measurements made.

Infrared spectrometry

The infrared spectrophotometer used was a Thermo Nicolette Nexus 870 e.s.p. FT-IR. All spectra were analyzed using OMNIC software. Spectroscopic measurements were conducted using PIKE Technologies Variable Angle Multi-Reflection ATR accessory. To conduct measurements a custom made cell was placed on top of the Si crystal. The IR-ATR spectrum of the polymer multilayered coating was taken as a background. An analyte was placed in a small Al bucket and was allowed to vaporize in the closed cell. After ten minutes passed, an IR-ATR spectrum was taken (32 scans) with resolution set at 4 cm^{-1} . Spectra of the analytes in the liquid phase were obtained by applying 1-4 drops of an analyte on a non-coated silicon crystal. (The purpose of the experiment was to obtain spectrum of a substance to show characteristic peaks for the qualitative comparison. Therefore, we did not control an amount of the substance placed and did not prevent an evaporation of the substance during the measurements.) Spectra of the analyte in the vapor phase using a non-coated silicon crystal were obtained as well. All spectra were smoothed in Origin Ver 6.1 by use of the FFT filtering operation using a polynomial of 3 and taking five points to either side.

Analytes detection with micro-disc resonators

Transmission spectra of the fabricated device have been measured on a Newport AutoAlign workstation in combination with a tunable laser (optical vector analyzer external laser, LUNA Technologies, Inc.). Lens-tip fibers were used to couple light from the laser into and out of the devices. Reproducible coupling was achieved via an automatic alignment system with a spatial resolution of 50 nm. The sample was mounted on a thermostat stage and kept at 25 °C for all measurements. Analyte was delivered in a small Al bucket placed near micro-disc resonator and enclosed with PDMS (polydimethylsiloxane) chamber. A series of transmission spectra were recorded until shift in the micro-disc resonance reached its maximum.

S2. Ellipsometry measurements

To determine if the multilayered coating is capable of acting as a “universal” enrichment layer, coating swellability in the presence of different analytes was tested. The swelling of the coating was monitored by ellipsometry. In fact, the nanostructured polymer film was capable of swelling to a certain extent with each analyte used in the study (**Figure S1**). Kinetics and amount of swelling was different for each analyte, some taking longer than 4000 seconds to reach equilibrium with analyte vapor.

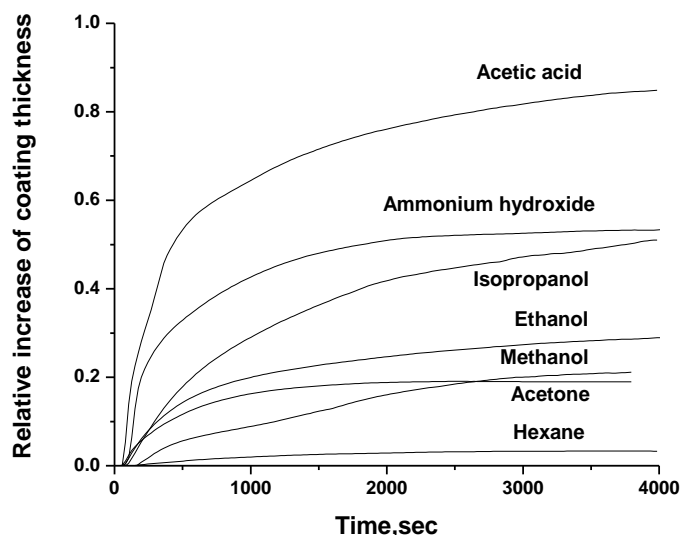
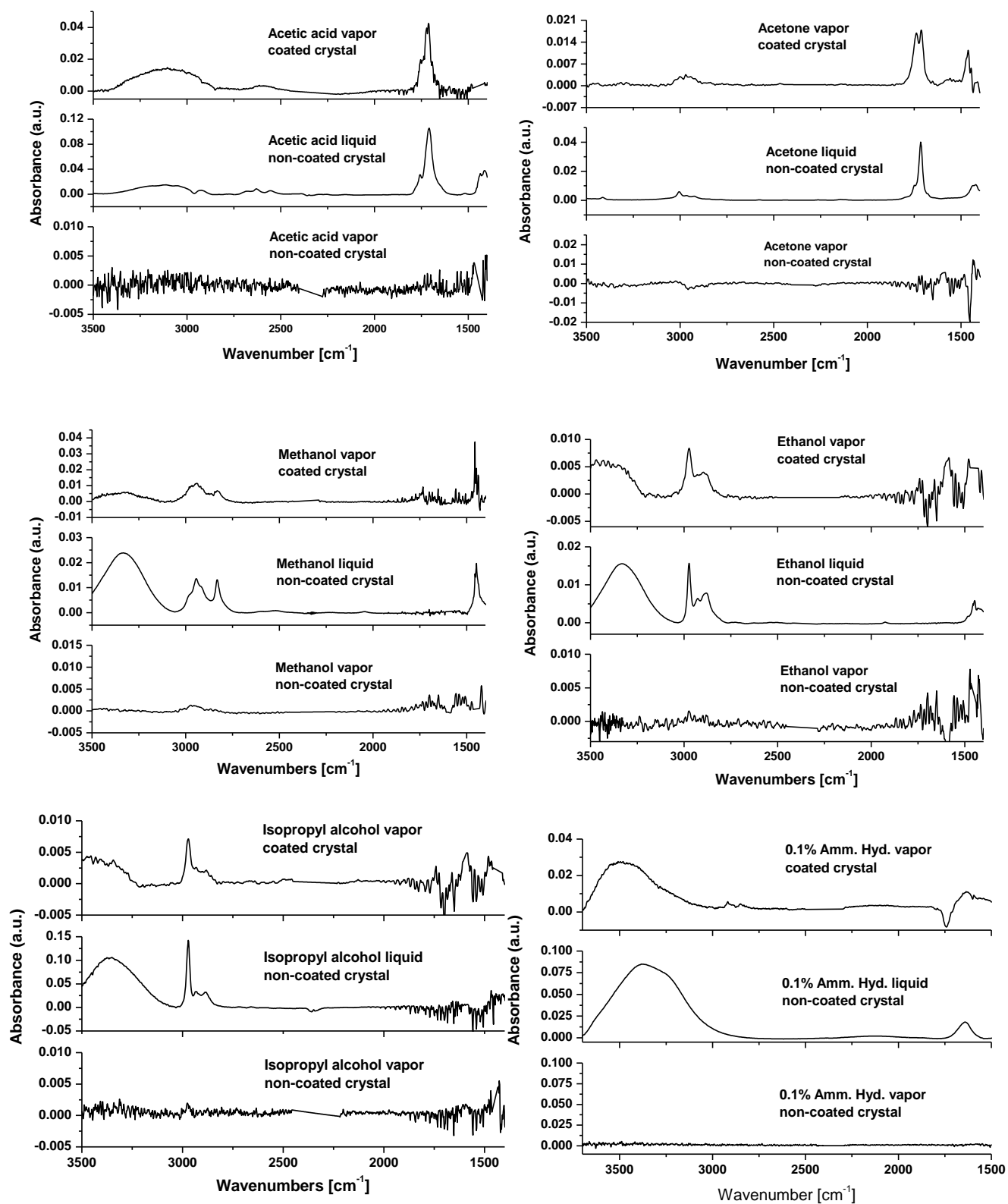


Figure S1. Relative change of the coating thickness in the presence of various analytes. Measurements were done with ellipsometry. Initial thickness of the nanocoating is ~27 nm.

S3. FT-IR measurements of each analyte with and without multilayer enrichment layer

IR-ATR spectra for vapors of seven different substances were recorded using Si crystal waveguide modified with the enrichment polymer film synthesized. Specifically, vapors of methanol, ethanol, isopropanol, acetone, acetic acid, hexane, and 0.1% ammonium hydroxide were analyzed. Obtained spectroscopic data clearly demonstrates that each substance was “picked-up” by the enrichment coating and produced unique signature allowing distinguishing between the analytes. Conversely, when unmodified Si crystal was used no spectroscopic signal was observed in the same conditions (**Figure S2**). For comparison for each analyte spectrum of the analyte in a liquid form is also presented.



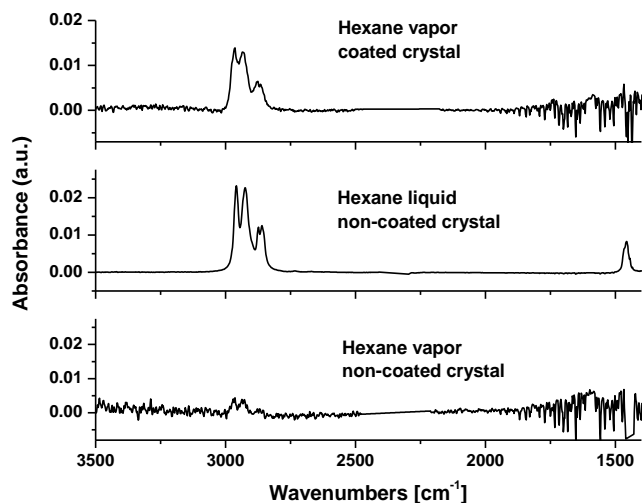


Figure S2. IR -ATR spectra of 7 analytes obtained using Si crystal covered with the multilayer enrichment coating. Spectra of liquid samples and analyte vapor obtained using Si crystal without the enrichment coating are also presented for comparison. IPA is an abbreviation for isopropyl alcohol.

S4. Repeatability of the multilayer enrichment layer detection

To verify that the multilayered coating can be used for multiple measurements repeatedly and IR-ATR signal depends on the concentration of an analyte vapor we conducted the following series of experiments. First of all, the saturated acetone vapor was pumped over the Si crystal covered with the coating followed by flushing with pure nitrogen stream. After IR-ATR signal returned to the baseline the crystal was exposed to acetone vapor again. In the next measurements the saturated vapor was mixed with pure nitrogen in different ratios and pumped over the coated crystal. Subsequent to the each measurement the cell was flushed with pure nitrogen until IR-ATR signal returned to the baseline. **Figure S3** shows area under carbonyl peak absorption for the four different dilutions of the acetone vapor. Three concentrations have two consecutive measurements with corresponding standard deviation while only one measurement was taken for 70 to 30. The measurements demonstrated that the multilayered coating can be used for multiple measurements and it is sensitive to the analyte concentration in the vapor phase.

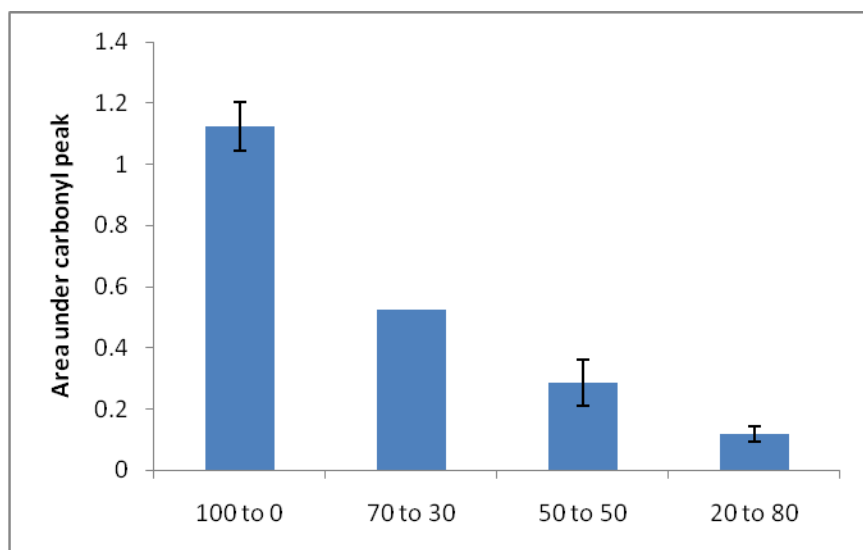


Figure S3. Result of the multiple IR-ATR measurements using Si crystal coated with the multilayered coating for acetone vapor of different concentrations. X-axis for each bar shows the ratio of saturated vapor to that of nitrogen gas in units of stream (mL/min).

S5. Acknowledgements

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