Supporting Information

Highly Sensitive, Label-Free Detection of 2,4-Dichlorophenoxyacetic Acid using an Optofluidic Chip

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Abstract:

The supporting information includes the description of chip fabrication process; schematic illustration of the sensing setup; real time monitoring of the resonance wavelengths of the 2,4-D-BSA functionalized microring resonator on sequence sensing of a variety concentration of monoclonal anti-2,4-D; noise analysis; calibration curve of resonance wavelength shift vs. concentration of monoclonal anti-2,4-D; and the fitting result of the dose response curve of the competitive immunoassay.

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The silicon photonic chip is fabricated by standard complementary metal-oxide-semiconductor (CMOS) fabrication process on silicon-on-insulator (SOI) wafer (Figure S1). The wafer has a 220-nm thickness silicon structure layer and a 2-μm thickness bottom silicon dioxide layer. First, 70-nm silicon dioxide layer is deposited on top as hard mask for etching. The waveguide and ring resonator structures are patterned by deep UV lithography and followed by reactive ion etching (RIE) process. Then the whole chip is covered with 2-μm thickness silicon dioxide for protective propose. In order to couple light from chip edge, an etched deep trench is formed at chip edge and then covered with 40-nm Al_2O_3. Then another lithography is used to form window pattern on Al_2O_3. Al_2O_3 is finally used as hard mask for following vapor HF release process to expose the silicon waveguide structures.

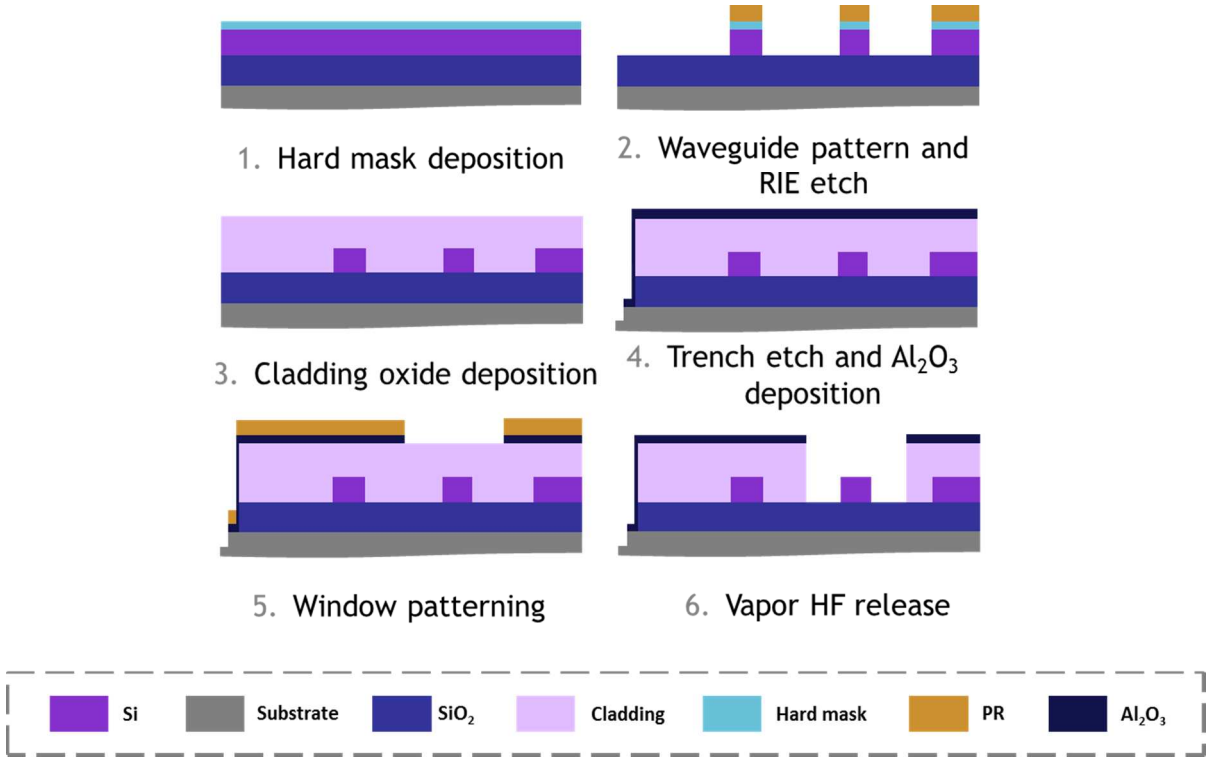

Figure S1. Fabrication process

A schematic drawing is provided in Figure S2, showing the excitation and the measurements of the signals. An ASE broadband source laser is coupled into the bus waveguide through a tapered lensed fiber. The polarization controller is employed to tune and select TE component of the light for injection into the waveguide. Subsequently, a tapered lensed fiber is used to couple the transmitted light out from the optofluidic chip and an Optical Spectrum Analyzer is used to capture the transmitted light spectrum with resonance wavelengths. The alignment of the fibers and the optofluidic chip is precisely controlled by the nano-positioning system.

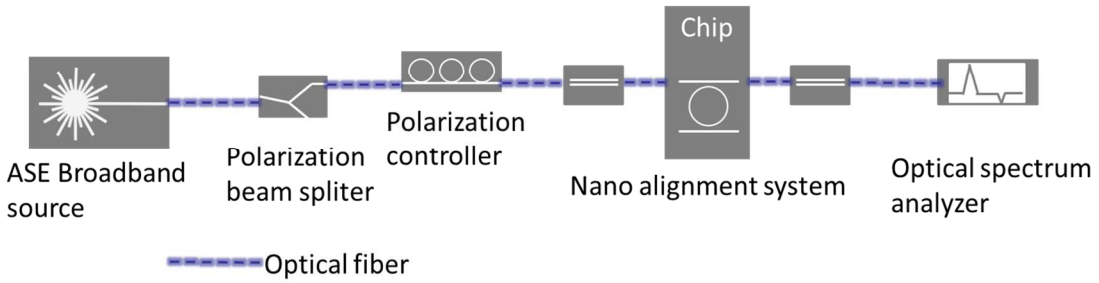

Figure S2. A schematic illustration of the sensing setup

The resonance wavelength of the 2,4-D-BSA decorated microring resonator optofluidic chip were monitored in real time. Monoclonal anti-2,4-D solutions in the concentration range 5 ng/mL to 500 μg/mL were injected in a random sequence. Figures S3 shows the resonance wavelengths of the functionalized microring resonator when exposed to a variety concentration of monoclonal anti-2,4-D.

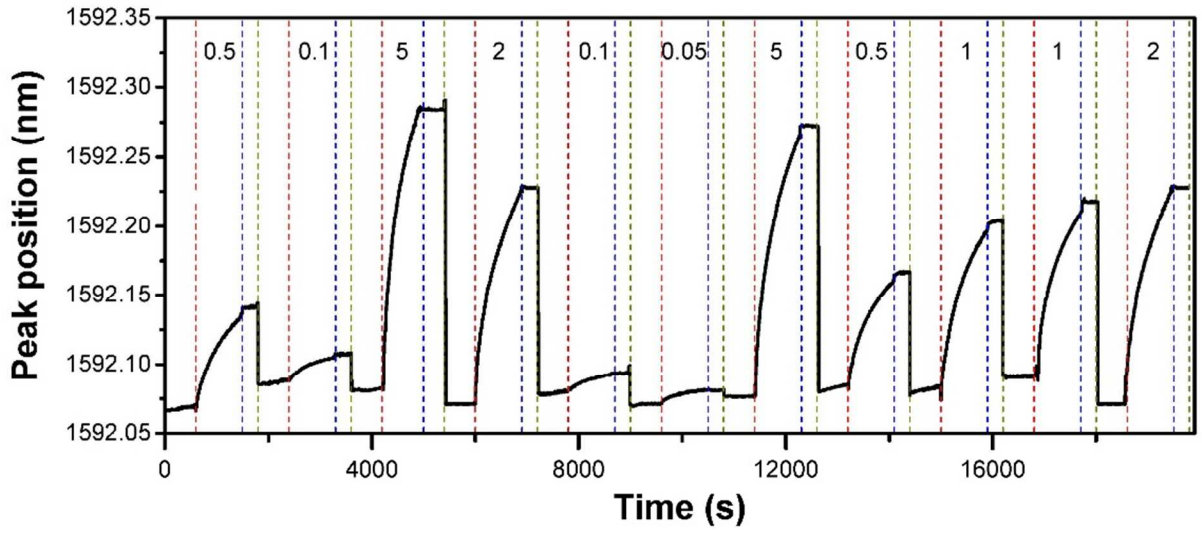

Figure S3. Real time monitoring of resonance wavelengths of the 2,4-D-BSA functionalized microring resonator on sequence sensing of a variety concentration of monoclonal anti-2,4-D (0.5, 0.1, 5, 2, 0.1, 0.05, 5, 0.5, 1, 1 and 2 μg/mL). 0.1mg/mL BSA in PBS was the running buffer, pepsin in glycin-HCl buffer serves as the regeneration buffer.

Figure S4 displays the response of the microring resonator that is exposed to a monoclonal anti-2,4-D solution at lower concentration.

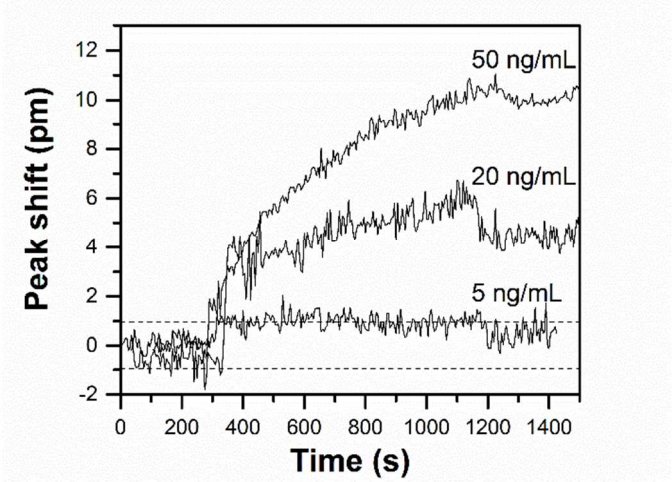

Figure S4. Resonance wavelength shift of the silicon photonic microring resonator immobilized with 2,4-D-BSA exposed with monoclonal anti-2,4-D at 5, 20 50 ng/mL. The dash lines represent the 3σ level (signal-to-noise ratio of 3).

The baseline of the optofluidic chip were recorded and the noise level were calculated (Figure S5). A signal-to-noise ratio of 3 is determined as 0.97 pm.

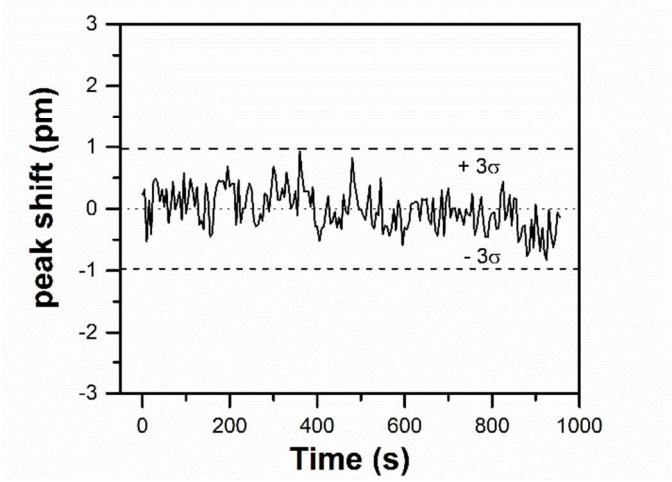

Figure S5. Baseline recorded during calibration buffer (BAS in PBS, pH=7.4) running.

In Figure S6, the resonance wavelength shifts are plotted vs. the antibody concentrations. At lower concentration, the shift increases linearly with the concentration of monoclonal anti-2,4-D (Figure S6 inset).

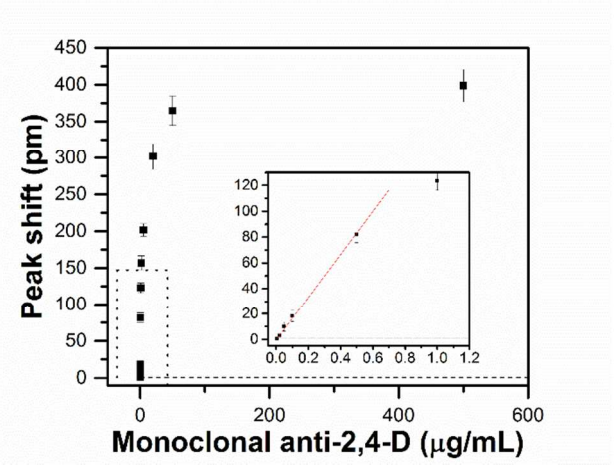

Figure S6. Plot of resonance wavelength shift vs. concentration of monoclonal anti-2,4-D, inset: at low concentrations.

Competitive immunoassay is used for the quantification of the 2,4-D. A calibration curve is shown in Figure 4. A sigmoidal curve was obtained. The curve was fitted to Eq. 2. The fitting results are shown in Table S1:

$$y = \frac{A_0 - A_1}{1+(\frac{[x]}{[x_0]})^p} + A_1, \qquad (2)$$

Table S1. The fitting results of the calibration curve of the competitive immunoassay.

Parameter	Value	Standard Error
A_0	1.05137	0.01751
A_1	-0.03068	0.04056
x_0	1332.53901	328.22623
p	0.39785	0.03333
Adj. R-square	0.99657	

According to reference 29, the LOD was calculated at 5 % inhibition. When y=0.95, x was calculated to equal 4.46 pg/mL. When y=0.90, x was calculated to equal 13.87 pg/mL. Thus, The LOD of this

competitive immunoassay based on silicon photonic microring resonator for 2,4-D is determined to be 4.5 pg/mL. The limit of quantification (LOQ) for 2,4-D (10 % of inhibition calculated from the calibration curve) is approximately 15 pg/mL.