

Supporting Information

“Millisecond kinetics of nanocrystal cation exchange using microfluidic X-ray absorption spectroscopy”

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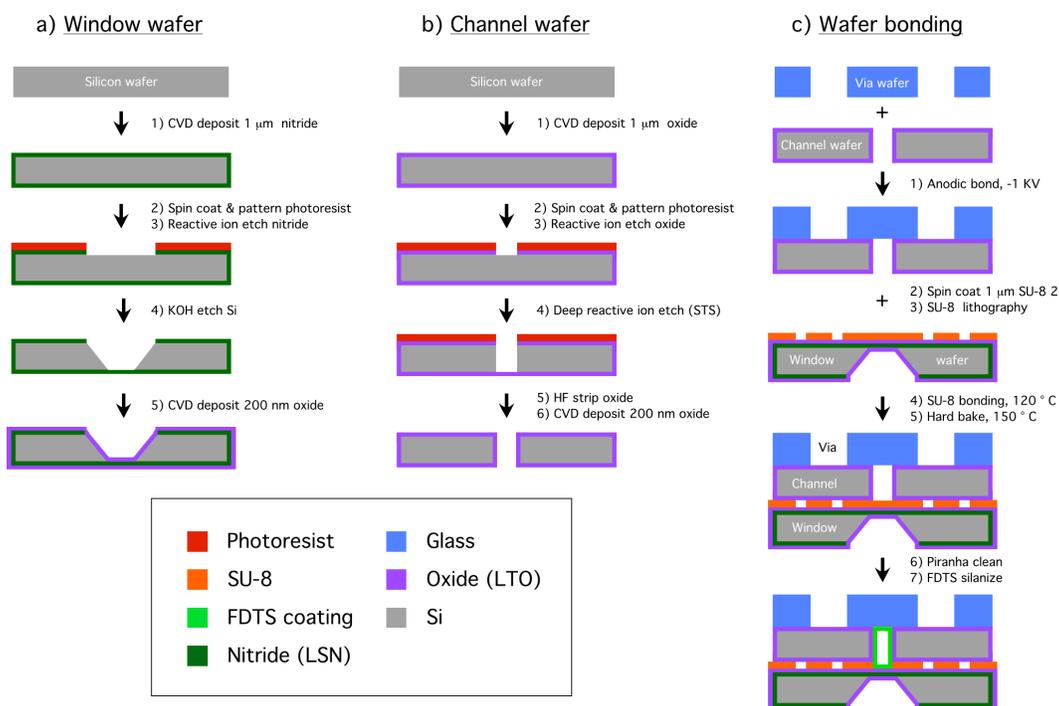


Figure S1. Chip fabrication process flow for (a) the window wafer, (b) channel wafer, and (c) wafer bonding.

Microchip Fabrication

The microfluidic X-ray absorption spectroscopy (XAS) device is fabricated as three separate layers: (1) a top, silicon “window” wafer, (2) a middle, silicon “channel” wafer, and (3) a bottom, glass “via” wafer. The fabrication process (Figure S1) is detailed below.

The window wafer is fabricated with 1 μm -thick silicon nitride windows that allow the sample to be probed with XAS with negligible window absorption (Figure S1a). Silicon (100) (430- μm thick, 100-mm diameter) wafers are coated with 1 μm -thick low-stress (silicon-rich) silicon nitride via chemical vapor deposition (CVD). Reactive ion etching (RIE) is used to remove the nitride corresponding to the window mask pattern, which is aligned to the wafer’s (110) planes. The exposed silicon is anisotropically etched with KOH through to the nitride on the back of the wafer. These resulting nitride membranes are protected with 200 nm of low-temperature CVD oxide (LTO) on each side.

The channel wafer contains etched channels for flowing the reaction solutions. Flow channels (43- μm wide) are lithographically etched completely through 403 μm -thick, double side-polished (DSP) silicon wafers using deep reactive ion etching (DRIE) and then passivated with 200 nm of CVD oxide (Figure S1b).

The via wafer, made from 575 μm -thick borofloat glass, contains drilled holes for fluidic access to the channel layer.

Bonding. The fluidic channels are enclosed by sealing the channel wafer between the window wafer and via wafer (Figure S1c). The glass via wafer is first anodically bonded to the bottom of the Si channel wafer. The nitride window wafer is then bonded to the top of the channel wafer using 1 μm -thick SU-8 photoresist. The epoxy resin-based SU-8 (Microchem) is chemically and mechanically robust when cured. Other bonding methods are avoided due to fragile nature of the nitride membranes. To perform the SU-8 bonding, standard procedures (1 min bake cycles, 93 mJ/cm^2 I-line dose, 30 s development) are used to lithographically pattern SU-8 2 on the membrane side of the window wafer. After rinsing with isopropyl alcohol and gentle drying, the SU-8 is baked on a 70 $^{\circ}\text{C}$ hot plate for 1 min and then at 90 $^{\circ}\text{C}$ for 5 min in order to remove volatile solvents. Using a Karl Suss BA6 wafer aligner, the window wafer is then aligned to the channel-via wafer assembly. Finally, the aligned wafers are bonded by pressing the SU-8 layer onto the exposed surface of the channel wafer. The bond is facilitated by placing the three-wafer stack on a 120 $^{\circ}\text{C}$ hot plate and rolling a cylindrical metal weight over the stack with manual pressure for ~ 5 min. This rolling action, in addition to the channels in the SU-8, helps to eliminate voids in the softened photoresist. The SU-8 is hard baked in an 150 $^{\circ}\text{C}$ oven for 1 hr, after which the bonding is robust enough to survive dicing of the devices.

Passivation. In order to prevent nanoparticle deposition on channel walls during the reaction, the oxide-coated walls are silanized with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) from solution.¹ A room-temperature piranha-cleaning step prior to silanization strips the SU-8 in the channel but not the SU-8 sandwiched between the wafers, demonstrating the chemical resistance of the bond.

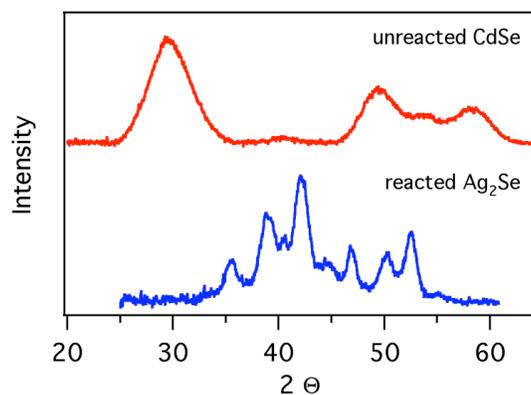


Figure S2. Powder X-ray (Co K α) diffraction patterns of unreacted and chip-reacted nanocrystals. The original CdSe nanocrystals (top) exhibit characteristic wurtzite CdSe peaks, while the product nanocrystals (bottom), reacted in the chip using 2.8 mM CdSe and 5 mM AgClO₄, exhibit only the peaks of tetragonal Ag₂Se.

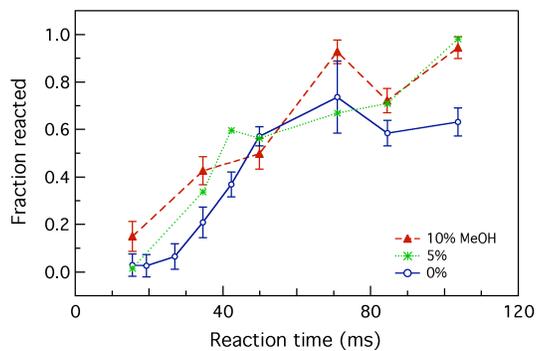


Figure S3. Fraction reacted vs. time with the indicated volume fractions of methanol at 2.8 mM CdSe, 5 mM AgClO₄.

References

- (1) Chan, E. M.; Alivisatos, A. P.; Mathies, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 13854.