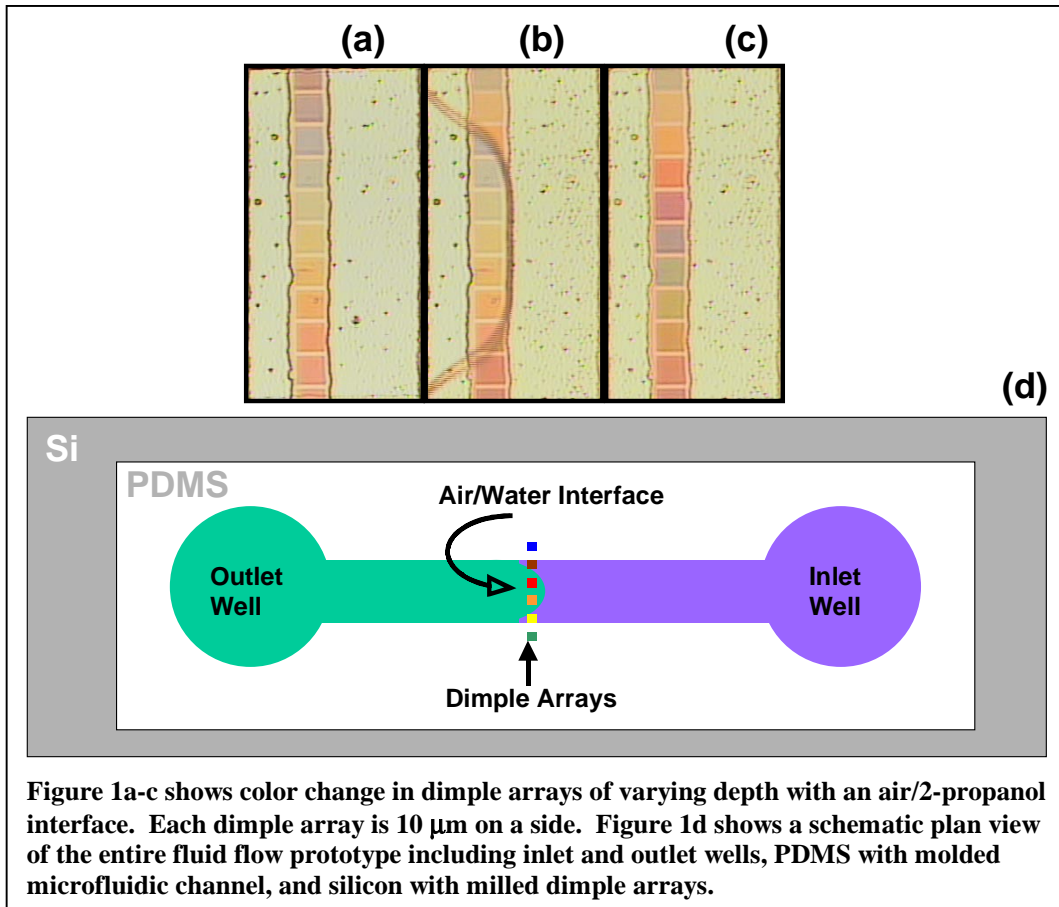**Supporting Information:**

In order to test nanofabricated array structures in a microfluidic channel, a prototype flow system was assembled[1]. A 75 mm diameter silicon wafer was used as a master for molding a polydimethyl siloxane (PDMS) channel. The silicon was thermally oxidized, and photolithographically patterned using Shipley 1813 photoresist purchased from MicroChem (Newton MA, USA) and a transparency mask purchased from Digital PageWorks (Cambridge MA, USA). The test pattern simply consisted of two 2 mm square wells connected by a 200 µm wide channel. This pattern was transferred into the thermal oxide using buffered hydrofluoric acid purchased from J. T. Baker (Phillipsburg NJ, USA). The photoresist was removed using a Caros acid solution mixed from hydrogen peroxide and sulfuric acid (J. T. Baker). The silicon was then bulk etched using potassium hydroxide (J. T. Baker) forming a 10 µm ridge for the microfluidic channel mold. Dow Corning Sylgard 184 Polydimethlsiloxane (PDMS) was mixed and deaired according to manufacturer specifications[2] and poured over the bulk micromachined silicon master with hollow cylindrical glass wells placed at the extents of the silicon ridge. The well walls are approximately 1 mm thick, 5 mm in diameter, and 20 mm in height. The entire assembly was cured at 150°C for 1 hour, and then the PDMS was peeled away from the silicon master with the glass wells intact. This technique resulted in a PDMS structure approximately 2-5 mm thick with a 10 µm deep channel between the two wells. This molded PDMS microchannel was then placed over dimple arrays fabricated on silicon wafers for fluid flow experiments.

The room temperature fluidic sealing of PDMS to silicon, and the simple method of removal and reapplication of the channel to silicon made alignment of the 200 µm wide channel to the 10 µm wide dimple arrays a matter of trial and error. The nanostructured arrays were easily observed in an optical microscope and it was noted that only a minor change in contrast was observed between arrays observed in air and arrays observed with PDMS channels over them, which was attributed to the nearly ideal transparency of the channel material. Wells were filled using a variety of liquids, some of which filled the channel through capillary action, and some of which required pneumatic actuation to fill the channel. Fluids tested included air, water, ethyl alcohol, methyl alcohol, isopropyl alcohol (alcohols obtained from J. T. Baker), and index matched fluids (Series A and AA, obtained from Cargille Labs, Cedar Grove NJ, USA). These fluids provided a wide range of refractive index as well as wetting properties. The channel and arrays were typically rinsed with solvent and dried in nitrogen between fluid flow experiments.

Figure 1a-c shows optical micrographs of dimple arrays under a PDMS channel with a 2-propanol/water interface over the top of the arrays. In 1a, the dimple arrays are covered by a channel filled with air, in 1b the water covers half of the arrays, and in 1c the arrays are completely covered in water. The entire prototype flow system is depicted schematically in 1d. One array in particular shows a striking change from blue to orange and this change is captured with the alcohol/air interface covering half of this array in 1b. For this setup the position of the air/water interface was controlled pneumatically, and the arrays were able to switch back and forth between the two colors easily.

After the air/liquid demonstration shown in Figure 1, a row of arrays was fabricated using parameters such that a striking change (between orange and blue) would

Figure 1a-c shows color change in dimple arrays of varying depth with an air/2-propanol interface. Each dimple array is 10 μm on a side. Figure 1d shows a schematic plan view of the entire fluid flow prototype including inlet and outlet wells, PDMS with molded microfluidic channel, and silicon with milled dimple arrays.

result when using the air/water system. These arrays were then placed under the fluidic channel described above with the row of arrays positioned lengthwise along the channel (rather then vertically across the channel, as depicted in Figure 1). Video 1 shows this row of dimple arrays undergoing several changes between air and water. Acquisition rate for digital video was set at about 100 milliseconds, or 10 frames per second. Each dimple array is 10 μm on a side.

Due to the similar refractive indices of most liquids, a difference in color was not easily observable for changes between water, ethanol, methanol, and 2-propanol, but significant changes were easily observed for fluid–to–fluid changes using index matched fluids. The color of the arrays used in Video 1 changed from orange to red when the Cargille Series A fluid replaced the water in the channel. Video 2 illustrates a demonstration of liquid–to–liquid operation of the channel. In this case a clear interface exists between water and Cargille AA fluid, so no mixing of the water and Cargille AA fluid occurs during the color change. Use of these arrays as a detection mechanism is more obvious in Video 3. The fluid–to–fluid interface is diffuse when using a Cargille AA–to–Cargille A system because these fluids do mix when flowing through the microchannel. A change in color for all fields shown indicates that Cargille A has replaced the Cargille AA fluid in the arrays even though an interface is not clearly observable. The color change is such that each field approximately assumes the color of the field to the right of it after about one minute. The change is complete after about 2

minutes. The only other indication of flow in the channel is a particle that passes just below the fields (from left to right) in the final seconds.

The time for the arrays to switch back to their original color was observed to vary when the arrays changed from water to air. We attribute this variation in switching time to buildup of water vapor in the channel. Even though PDMS is highly hydrophobic, over time the channels accumulated particulate contaminants that we believe contributed to moisture buildup in the channel. Also, silicon with native oxide is hydrophilic, which further contributes to moisture buildup. Due to these effects, the variation in time for switching colors from water to air is attributable to varying conditions related to thermal evaporation.

The length of time required for the arrays to change color was not constant for different liquids. For all cases where a liquid / air interface was used, the arrays changed color instantaneously (to the resolution of this technique) when switching from air to liquid. When switching from liquid back to air, the switching time ranged from nearly instantaneous to several days. When switching from water or 2-propanol to air, the time was always less than one minute. Using methanol, the switching time was observed to go on for very long periods of time even after the PDMS channel was removed from the silicon; in fact, the only ways to get the arrays to switch back to their original color were to either raise the temperature to 90°C for several seconds, or replace the methanol with another liquid with a thorough rinsing. We believe that this variation in time is due to surface energy differences between the liquids in the arrays and not due to thermal evaporation. However, since elevated temperature was able to induce the change in all cases, switching may be accomplished using a thermally resistive heater integrated underneath the optical plane.

References:

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2. Product Information, SYLGARD® 184 Silicone Elastomer, Dow Corning, 1998.