Creation and Perturbation of Planar Networks of Chemical Oscillators

Nathan Tompkins,[1] Matthew Carl Cambria,[1] Adam L. Wang,[1] Michael Heymann,[1] and Seth Fraden[1]
Physics Department, Brandeis University, Waltham, Massachusetts, 02453

I. SUPPLEMENTAL METHODS

The following sections detail the methods used to create our devices and are intended to assist those who wish to implement their own planar networks in a BZ emulsion system. The experiments described here use a BZ formulation with final concentrations of 400mM Malonic Acid, 80mM Sulfuric Acid, 300mM Sodium Bromate, 10mM Sodium Bromide, 3mM Ferroin, and 1.2mM Rubpy. Some experiments used slight variations on this formulation with concentrations of 640mM Malonic Acid, 2.5mM Sodium Bromide, and/or 0.4mM Rubpy. These variations are minor as within these concentration ranges the only noticed effects are slight variations in period, initial transients, and photosensitivity.

A. Close-Packed BZ Emulsion

The BZ emulsion is created using a typical flow-focusing microfluidic device with surfactant (RAN Biotechnologies FluoroSurfactant) stabilized oil (3M^{TM} Novec^{TM} 7500 Engineered Fluid) and collected in an Eppendorf tube. An approximately 1cm length piece of 2mm$\times$100μm rectangular glass capillary (VitroTubes^{TM}) is cut with a diamond scribe. The cut piece is held in forceps and one end is inserted into the emulsion. Capillary action is sufficient to fill the capillary. After the capillary is entirely filled leaving no air gaps, the ends are dipped in epoxy (Bob Smith Quik-Cure^{TM} five minute epoxy) and placed flat on a microscope slide. It is important to seal the capillary gas tight otherwise CO_2 bubbles form which displace the oil, quench the oscillation, and move drops. More epoxy is carefully applied to the ends of the capillary to attach it to the slide. The portion of the capillary to be imaged remains clear of epoxy. After the epoxy has cured, the slide is placed in the microscope for experimentation.

B. Thin PDMS Devices

The thin PDMS devices are created using a four step process. The first step is to create a photoresist master on a silicon wafer with the desired features in inverse using standard photolithography methods.

The second step is to create a PDMS cast of the silicon master as shown in Fig. S.1(a) where the silicon master is placed in a specially designed frame that allows for the curing of 40-50g of PDMS (Dow Corning SYLGARD® 184 Silicone Elastomer Kit mixed using a Thinky® planetary non-vacuum centrifugal mixer) to create an inverse

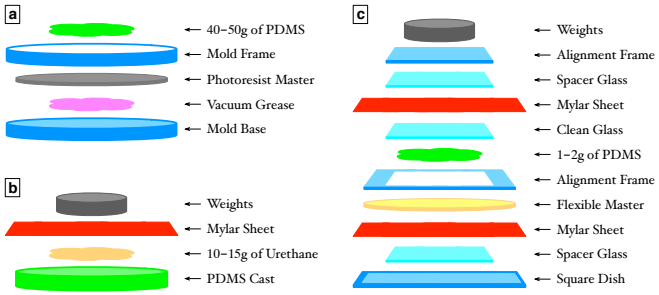

FIG. S.1. Schematic illustrations of the steps to make thin PDMS devices. **a)** Making a PDMS cast of a silicon master. A photoresist master on a silicon wafer with the desired features in inverse is prepared by traditional photolithographic methods and attached to a hard plastic disk (mold base) with silicone based vacuum grease. An outer containment frame is attached and 40-50g of PDMS are poured over the top. After degassing and curing, the PDMS cast can be removed from the frame and detached from the silicon master. **b)** Making a flexible plastic master from a PDMS cast. A PDMS cast of the desired features is filled with 10-15g of plastic urethane resin and thoroughly degassed. After degassing, the resin is covered with a protective mylar sheet and pressed flat with weights. After curing, the flexible master can be removed from the PDMS cast. **c)** Preparing a thin PDMS device from a flexible plastic master. A flexible plastic master with the desired features in inverse is placed in a square dish on top of a protective mylar sheet and a glass spacer. A laser cut alignment frame is placed over the flexible master and aligned with the features. 1-2g of PDMS are poured over the features and degassed. While degassing, a glass slide is freshly plasma cleaned and then placed on the degassed PDMS, snugly fitting within the alignment frame. Another protective mylar sheet is placed over the clean glass followed by another glass spacer, the top of the alignment frame, and flat weights. The entire stack is further degassed before curing. After curing, the stack is carefully disassembled as the PDMS has cured onto the clean glass. See supplemental videos for more.

cast of the silicon master. The frame consists of a stable base and a circular outer ring. When bolted together the two parts of the frame contain the fluid PDMS. The silicon master is adhered to the base of the frame using silicone based vacuum grease. After curing, the mold frame is removed and the PDMS cast is peeled off of the silicon master.

The third step is to create a flexible plastic master with the desired features in inverse using the PDMS cast of the silicon master as shown in Fig. S.1(b). 10-15g of urethane resin (Smooth-On Crystal Clear® 204 urethane casting resin mixed using a Thinky® planetary non-vacuum centrifugal mixer) is prepared and poured into the PDMS cast. Special care needs to be taken to thoroughly degas the resin as it is very viscous and prone

to retaining bubbles. After degassing, the resin is pressed flat within the PDMS cast using flat-bottomed weights. A mylar sheet is placed between the resin and the weights to prevent the resin from adhering. After curing, the flexible master can be peeled off of the PDMS cast.

The fourth step is to create the thin PDMS device using the flexible plastic master as shown in Fig. S.1(c). The flexible master is placed in a square dish on top of spacer glass and a mylar sheet. The spacer glass creates a space for excess PDMS to drain into and the mylar sheet prevents the PDMS from adhering to the plastic dish. A laser cut alignment frame is placed over the flexible master and the master is positioned so that the features are aligned with the frame. 1-2g of PDMS are poured over the features and degassed. While degassing, the glass microscope slide that will carry the thin PDMS device is freshly plasma cleaned. The glass slide is taken directly from the plasma oven and placed immediately onto the degassed PDMS. This step and the composition of the glass (Gold Seal^{TM}) has shown to be critical to prevent the PDMS from later peeling off of the glass carrier. Another mylar sheet is placed over the carrier glass followed by another spacer glass, the top piece of the alignment frame, and flat-bottomed weights. The applied wights will squeeze excess PDMS into the space at the bottom leaving only a very thin layer on the carrier glass. The exact thickness of this layer will depend on the viscosity of the PDMS fluid and the weight applied. The assembled alignment frame prevents any relative movement between the PDMS and the carrier glass as the alignment frame is laser cut so that the carrier glass fits snugly within the alignment frame. The entire stack is further degassed before the PDMS is cured. After curing, the stack is carefully disassembled and excess PDMS is cut from the outside of the carrier glass/flexible master sandwich. The last step of the disassembly is to carefully peel the flexible master off of the carrier glass.

C. Etched Silicon Devices

The etched silicon chips are created using standard DRIE technology which is a four step process. The first step is to create a silicon master with the desired features using positive resist. It is critical that positive resist that can be washed off post-curing with acetone is used.

The second and third steps are carried out repeatedly within the DRIE machine. The second step applies a nearly isotropic plasma that etches exposed silicon but does not etch the positive resist. The third step applies an inert passivation layer that protects the entire surface. The second step is then repeated and the passivation layer is etched away but, due to the directionality of the plasma, the passivation layer is preferentially etched vertically thus protecting vertical edges and preventing undercutting. The second and third steps are continually repeated until the desired etch depth is reached. The iterative process leaves the vertical edges scalloped, but the degree of scalloping is tunable by adjusting the duration of the etch step.

The fourth step is to wash off the positive resist using an acetone bath. If needed, acetone residue can then be washed off using an isopropanol bath. After washing, all applied materials will have been removed except for possibly passivation residue on the vertical edges of the etches.

D. Top-Loaded Devices Clamping

The thin PDMS and etched silicon devices are used in experiments by clamping a cover slide onto the features. The two devices use slightly different clamps as can be seen in Fig. S.2.

The clamp for the thin PDMS devices has optical access holes on the top and bottom to allow for transmission illumination. The thin PDMS carrier glass is placed on a backing glass for support. The thin PDMS is wetted with oil to prevent air bubbles from being caught in the features. The BZ emulsion is then pipetted onto the features and a cover slide is placed on top. The top of the frame is lowered and pressure is applied by tightening the frame screws.

The clamp for the etched silicon devices has an optical access hole only on the top, as the wafer is opaque so the device must be imaged in reflection only. The silicon device is placed directly in the lower portion of the frame and wetted with oil to prevent air bubbles from being caught in the features. The BZ emulsion is then pipetted

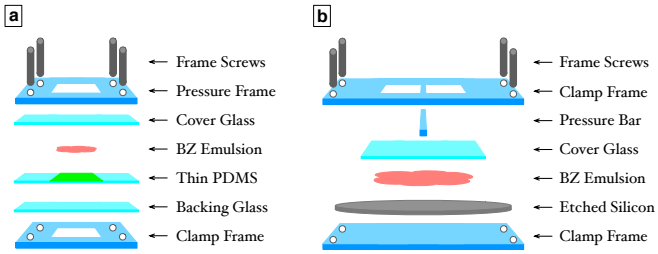

FIG. S.2. Schematic illustrations of the device clamps. **a)** Thin PDMS device clamp. The thin PDMS device is placed onto a backing support glass on the bottom of the clamp frame. These devices are imaged using transmission illumination so the top and bottom of the clamp have optical access holes. The BZ emulsion is placed on the device and covered with a cover slide. The top of the clamp is lowered onto the cover slide and the screws are tightened to apply pressure. **b)** Etched silicon device clamp. The etched silicon device is placed onto the bottom of the clamp frame. These devices are imaged using reflection illumination so only the top of the clamp has an optical access hole. The BZ emulsion is placed on the device and covered with a cover slide. A plastic bar is placed under the cross bar of the top of the clamp so that pressure is applied from the center. The top of the clamp is then lowered and the screws are tightened to apply pressure. See supplemental videos for more.

onto the features and a cover slide is placed on top. A plastic bar is placed under the cross bar of the top of the clamp so that pressure is applied to the device from the center to prevent buckling. The top of the clamp is then lowered and pressure is applied by tightening the frame screws.

II. VIDEO CAPTIONS

Video 1a - Optical isolation of a single drop of BZ. Halfway through the video optical inhibition (not seen) is applied to all drops except the center. The center drop continues oscillating while all the others stop. Video at 135x real time. Drop diameters are 150m.

Video 1d - Optical isolation of a neighboring pair of BZ drops. All unlabeled drops are optically inhibited (inhibition not seen). The labeled drops start in phase and quickly become anti-phase. The phases of the two drops are shown on the right relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 1g - Optical isolation of a diagonally neighboring pair of BZ drops. All unlabeled drops are optically inhibited (inhibition not seen). The labeled drops start in phase and slowly drift apart and back again. The phases of the two drops are shown on the right relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 1j - Optical isolation of a second neighboring pair of BZ drops. All unlabeled drops are optically inhibited (inhibition not seen). The labeled drops start in phase and slowly drift apart. The phases of the two drops are shown on the right relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 3a - Physical isolation of a ring of seven BZ drops in thin PDMS. The drops start in phase and quickly form a heptagramoidal pattern. On the left lines are superimposed to indicate the order of oscillation. In the middle color coded circles correspond to the phases of the drops shown on the right. Phases are plotted relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 3c - Physical isolation of a ring of seven BZ drops in etched silicon. The drops start in phase and quickly form a heptagramoidal pattern. On the left lines are superimposed to indicate the order of oscillation. In the middle color coded circles correspond to the phases of the drops shown on the right. Phases are plotted relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 4a - A ring of three BZ drops isolated optically (top), in thin PDMS (middle), and in etched silicon (bottom). The drops start in phase and drift to form a triangular pattern. On the left lines are superimposed to indicate the order of oscillation. In the middle color coded circles correspond to the phases of the drops shown on the right. Phases are plotted relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 4b - A ring of four BZ drops isolated optically (top), in thin PDMS (middle), and in etched silicon (bottom). The drops start in phase and drift to form two anti-phase phase clusters. The phases of the drops are shown on the right relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 4c - A ring of five BZ drops isolated optically (top), in thin PDMS (middle), and in etched silicon (bottom). The drops start in phase and drift to form a pentagramoidal pattern. On the left lines are superimposed to indicate the order of oscillation. In the middle color coded circles correspond to the phases of the drops shown on the right. Phases are plotted relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 4d - A ring of six BZ drops isolated optically (top), in thin PDMS (middle), and in etched silicon (bottom). The drops start in phase and drift to form two anti-phase phase clusters. The phases of the drops are shown on the right relative to the average period. The white circle indicates zero phase. Video at 100x real time. Drop diameters are 150m.

Video 6a - Close-packed BZ drops are initially optically inhibited and released simultaneously to produce in-phase oscillations. The drops are later optically inhibited again and re-released simultaneously to reproduce in-phase oscillations. Video at 200x real time. Drop diameters are 150m.

Video 6b - Twelve drops of BZ are optically isolated from a close-packed system and illuminated with inhibitory light below the threshold required to prevent oscillations to measure the period elongation. The bottom four receive no inhibitory illumination to measure the control period, the middle four receive high illumination, the top four receive middling illumination. Periodically the intensity of illumination is incremented. Video at 500x real time. Drop diameters are 150m.

Video 6d - Twelve drops of BZ are optically isolated from a close-packed system and perturbed with pulses of inhibitory light at specified phases to measure the phase response curve. Video at 100x real time. Drop diameters are 150m.

Video S1a - A documentary video demonstrating how to make a PDMS mold of a silicon master.

Video S1b - A documentary video demonstrating how to make a plastic master from a PDMS mold.

Video S1c - A documentary video demonstrating how to make a thin PDMS device from a plastic master.

Video S2 - A documentary video demonstrating how to load and clamp an etched silicon device.