Supplementary Information
for
A Switchable Digital Microfluidic Droplet Dye-Laser

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Materials

The fluorescent dyes coumarin-450 (C-450), pyrromethene-556 (PM-556) and 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) were purchased from Exciton. The laser-dye solutions were prepared by dissolving C-450 (0.5 gL^{-1}) and DCM (2gL^{-1}) in DMSO (purchased from Sigma-Aldrich). PM-556 (2 gL^{-1}) was dissolved in milli-Q water. Reagents used for microfabrication included Shipley 1811 photoresist, Microposit 251 developer and Microposit Remover 1165 (from Rohm and Haas).

DMF-Device Fabrication and Operation

Digital microfluidic devices were fabricated in the Center for Nanoscale Systems (CNS) cleanroom at Harvard University. Bottom plate substrates were manufactured by e-beam evaporation of 5 nm chromium followed by 300 nm silver (for the bottom plate) onto glass microscope slides. An array of 116 actuation electrodes (2.2 x 2.2 mm ea.) connected to 10 reservoir electrodes (4 x 4 mm ea.) (with inter-electrode gaps of 30-80 μm) was patterned using photolithography. Briefly, Shipley 1811 was spin-coated, prebaked, exposed through a shadow mask with the electrode array design and developed in Microposit 251 in accordance with Shipley guidelines. The silver and chromium were then etched by immersing the substrates in a 1:1 mixture of ammonium hydroxide (30% in water) and hydrogen peroxide (30% in water) for 15 s, and a solution of ceric ammonium nitrate (16%) in aqueous nitric acid (6%) solution for 1 min, respectively. The photoresist was then stripped with Microposit Remover 1165.

For most experiments, an unpatterned substrate formed from 5 nm chromium and 30 nm silver on a glass slide (formed by e-beam evaporation as above) served as a top plate. In experiments used for visualization (i.e., for Fig. 2 and in the movie included in the online supplementary information), the top plate was formed instead from indium tin oxide (ITO) coated glass microscope slides (Delta Technologies Ltd). Prior to assembly, top and bottom substrates were coated with 12.7 μm thick Teflon FEP using a few drops of 20 cSt silicone oil (Sigma-Aldrich) for conformal adhesion. Devices were then assembled with a top and bottom plate separated by spacers formed from 100 μm diameter silica beads, such that ”unit” droplets (i.e., the droplet size covering a single actuation electrode) were 500 nL. The silica beads were applied at the edges of the bottom plate using a spatula and the top plate was gently pressed onto the bottom plate to achieve a monolayer of spacer beads. The top plate was secured in place using adhesive tape.

The laser-dye solutions were dispensed into the reservoirs on the DMF chip with a pipette, using capillary forces to pull into the gap between the two plates. To actuate droplets, driving potentials (350 V_{pp}) were generated by amplifying the output of a function generator (Agilent Technologies) operating at 18 kHz. Droplets were sandwiched between a patterned bottom plate and an unpatterned top plate and actuated by applying driving potentials between the top electrode (ground) and sequential electrodes on the bottom plate via the exposed contact pads.

DMF Dye-Laser Operation

The 355 nm emission line (3rd harmonic) from a pulsed q-switched Nd:YAG laser (Spectra Physics, GCR-230, pulse duration 5 ns, repetition rate 10 Hz) served as the optical pump for the dye laser. This beam was reflected off a 400 nm long pass filter and guided to the back aperture of a 4x microscope objective (Edmund Optics) which focused the pump light onto the semi-transparent unpatterned top plate of the DMF device. Using a micro-positioning stage, the device was positioned such that the beam was aligned to the center of the dedicated laser site. When a droplet of laser dye was manipulated into the laser site, the emission from the cavity was collected through the same objective, separated from any reflected pump light by the long pass filter, and focused onto the 20 μm entrance slit of a spectrograph equipped with a CCD camera (Andor Technology) with a 150 mm achromatic lens. The pulse energy delivered to the DMF device was adjusted by changing the q-switch delay of the Nd:YAG laser.

Reflectance Modeling

Reflectances of both silver films are shown in Fig. S1 and were computed using the well-established characteristic matrix approach that provides reflectance and transmittance of multilayer stacks of thin films (E. Hecht, Optics (4th Edition), Addison Wesley, San Francisco).

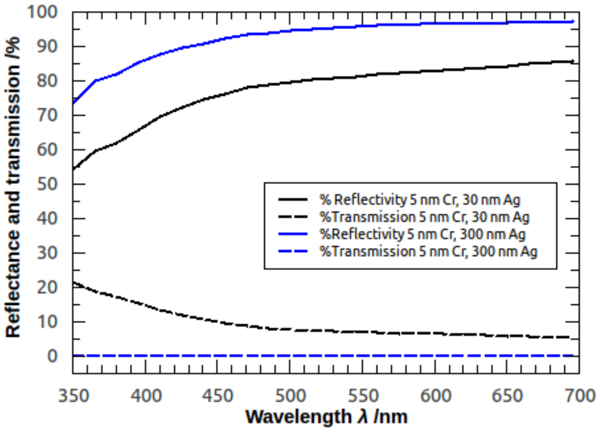

Fig. S 1 Reflectance and transmission spectra modelled for films consisting of 5 nm chromium and 30 nm or 300 nm of silver on glass.