Arrayed electrowetting microwells

K. Zhou and J. Heikenfeld[a)]
Novel Devices Laboratory, Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221, USA

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Colored oils and aqueous solutions have been electromechanically pumped in and out of arrayed microwells. The microwells comprised pyramidal pits in Si substrates that were coated with an aluminum electrode and a hydrophobic dielectric. These substrates were then suspended between volumes of water and oil. When colored oil was placed behind the substrate, surface tension forces caused the oil to completely fill the microwells and provide brilliant red coloration to the array. With application of ~30–50 V, electrowetting drove the colored oil behind the substrate and the reflection was made dominantly white. © *2008 American Institute of Physics*.
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Arrayed electrowetting[1] display pixels were first reported in 2003 by Hayes and Feenstra.[2] These pixel structures utilize a parallel plate capacitor configuration of water/colored-oil/hydrophobic dielectric/electrode. At no voltage, interfacial surface tension forces between the water/oil/dielectric result in a water contact angle θ_Y of ~170°. Therefore, the oil which has a very small complimentary contact angle of ~10°, is spread across the surface and provides coloration. Applying voltage to this system causes the water to electrowet the hydrophobic dielectric, the oil contracts to ~20% of its original area, and surface coloration is thereby altered.[3] Challenges for these devices include limited contrast ratio (i.e., the oil is always visible on the surface) and a short optical absorption length of ~5 μm in display resolution pixels (~100 μm). These challenges limit the white-state reflectance and the colored-state saturation, respectively. Reported herein is a novel structure consisting of arrayed microwells. As shown in Fig. 1, electrowetting is utilized to drive colored liquids in and out of microwell arrays and result in vivid change in the perceived surface coloration. These devices provide a simple means to provide tunable color surfaces, and may prove additionally useful for switchable retroreflectors or photonic crystals. First presented herein are fabrication and experimental details. Next, electrowetting and optical characteristics as a function of voltage are reviewed. Lastly, brief speculation on possible applications and future challenges are discussed.

A variety of techniques, such as microreplication, can be utilized to create microwells of tens to hundreds micrometer size in white plastic composites. Solely for purpose of simplicity, Si micromachining was utilized to create the microwell arrays tested herein. 500 μm thick (100) Si wafers were first patterned with a square grid of thermal oxide on the front of the wafer and a continuous coating of oxide on the backside of the wafer. Next, a highly Si/SiO_2 selective 25% tetramethylammonium hydroxide etch solution was utilized to anisotropically etch pyramidal microwells into the Si substrate. The process was carried out in a temperature controlled oil bath at 75 °C and with a cooling top to prevent evaporation of the etchant. The etch process was allowed to progress through the entire wafer and provided sloped (111) sidewalls of 54.7°. The resulting microwells were ~850 μm wide on the front side. After microwell formation, the remaining thermal oxide was removed in buffered oxide etchant. Next, an ~80 nm Al reflector was evaporated onto the wafer. To provide a dielectric for electrowetting operation, ~1 μm of Parylene C ($\varepsilon_r \sim 3$, $E_{bd} \sim 2$ MV/cm) was deposited using a Specialty Coating Systems 2010 Lab-Coater. This process involves dimer vaporization, vapor pyrolysis, followed by room-temperature monomer deposition and polymerization on the substrate surface at ~0.1 Torr. To impart proper hydrophobicity on the surface, the sample was dip-coated with Cytonix Corp. FluoroPel 1601 V solution, and baked at 120 °C for 20 min to form a ~0.1 μm thick

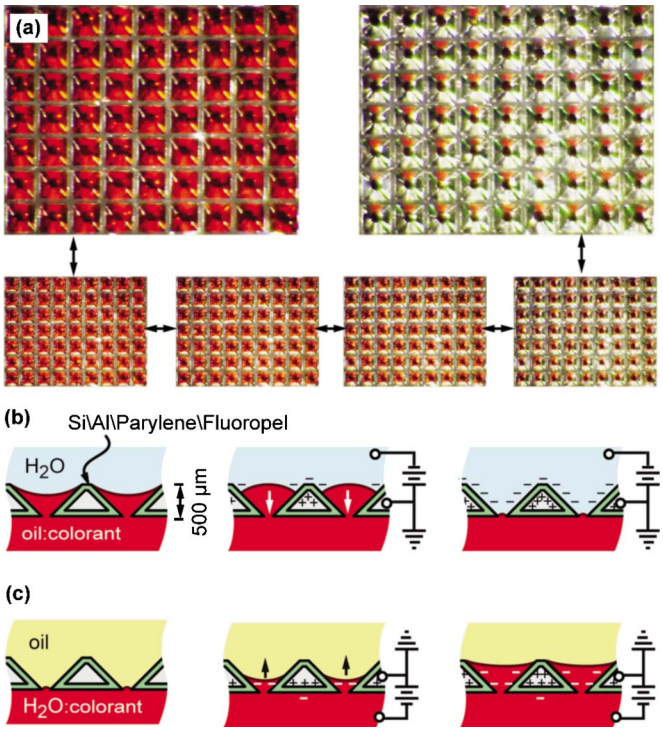


FIG. 1. (Color online) Operation of electrowetting microwells: [(a) and (b)] photographs and diagrams of operation with colored oil; and (c) diagrams of operation with colored water. A 3 mm capillary (not shown) was connected at the outside edge of the two liquid volumes to allow liquid counter flow during operation. See Ref. 12 for supplemental videos of operation for Figs. 1(b) and 1(c).

[a)]Electronic mail: Jason.c.heikenfeld@uc.edu.

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hydrophobic film with a surface energy of ~14 mN/m. Colored liquids were created utilizing coloration of dodecane, or de-ionized (DI) water, using colorants common to electrowetting display commercialization.[4] In conventional electrowetting display devices, a large ~10 wt. % of dye is needed to color ~5 μm thick oil films. In this work, the optical path length in the pyramidal structure is tens to hundreds of micrometer and only ~0.1 wt. % of colorant was required. Therefore, the interfacial surface tension of the liquids is close to that of pure dodecane and DI water (~50 mN/m). As shown in Fig. 1, device testing was performed by providing oil/water on either side of the substrate. Photographs and reflection spectra were taken using a uniform white diffuse illumination source. In all experiments, negative dc voltages were applied to the water with the Si wafer and the Al film held at electrical ground.

Turning attention back to Fig. 1(a), at zero voltage the contact angle for the oil/water is Young's angle (θ_Y ~160°–170°). Therefore, at zero voltage the water will exhibit a convex meniscus at any position in the microwell. Since the water has higher surface tension than the oil ambient, a net Young–Laplace pressure[5] is oriented toward the water phase according to $\Delta p = 2\gamma_{LA}/R$, where γ_{LA} is the water/oil interfacial surface tension of ~50 mN/m and R is the radius of curvature for the meniscus. Given the sidewall slope of 54.7° the Young Laplace pressure can be further expressed as a function of contact angle as

$$\Delta p = \frac{2\gamma_{LA}\sin(125.3° - \theta)}{h/\tan 54.7° + w/2}, \quad (1)$$

where new terms include the contact angle (θ), the vertical distance or height (h) of the contact line from the bottom of the microwell, and the width of the microwell at the bottom aperture (w). The smaller the microwell, the larger this pressure, and for a given microwell size the zero-voltage pressure is maximum at the smaller bottom aperture and minimum at the larger upper aperture. Since Young–Laplace pressure was adequate to overcome contact-line pinning and provide complete oil filling of the 850 μm size microwells tested herein, complete oil filling is therefore expected for all smaller size microwells as well. Any coloration of the microwell in this off state can be achieved by proper selection of the colorants within the oil. It should be further noted that no matter what the value of the water/oil contact angle (θ), the water/oil contact line will not recede or advance past the upper *or* lower rims of the microwell. This is because beyond the rims the contact angle (θ) would then be relative to the flat top or bottom surface of the substrate and the system would exhibit a Young–Laplace pressure directed toward the channel (i.e., the contact line being held within the microwell represents a local energy minima).

To alter the coloration of the microwell, the oil can be driven to the bottom of the microwell via electrowetting. Electrowetting modulates the macroscopically observed contact angle according to

$$\cos\theta_V = \cos\theta_Y + \frac{1}{2}\frac{\varepsilon V^2}{\gamma_{LA} d}, \quad (2)$$

where new terms are the dielectric capacitance per unit area (ε/d, F/m^2) of the hydrophobic dielectric, the applied dc voltage or ac rms voltage (V) and the *macroscopically* observed electrowetting contact angle (θ_V). It was first proposed by Jones[6] and later confirmed by Mugele and Buehrle[7] that during electrowetting the microscopic angle always remains Young's (θ_Y) and the electrowetting contact angle (θ_V) does not manifest until a distance from the contact line roughly equivalent to the hydrophobic dielectric thickness. This is noted for this work because the force driving the oil downward in the microwell should be considered as *electromechanical*. Therefore, Eqs. (1) and (2), while conveniently predictive, should be used knowing that electrowetting driven fluid flow should not be interpreted as due to contact angle change. The contact angle versus voltage response of the materials tested herein is shown in Fig. 2. Also shown in Fig. 2 is experimental lower voltage result that can be achieved if one utilizes sodium-dodecyl-sulfate (SDS) surfactant and a higher capacitance hydrophobic dielectric of ~100 nm Al_2O_3 and ~50 nm of Asahi Cytop fluoropolymer. It should be noted that the operating voltage for the microwells is theoretically *independent* of microwell size. Therefore, the results shown in Fig. 2 should be predictive for all practically achievable device sizes (i.e., approximately millimeters to micrometers). The diagrams at the top of Fig. 2 also show that the ideal threshold for driving the oil flow is when the voltage level results in a dominantly flat water/oil meniscus. This is an ideal case for the threshold, because in practice, contact line pinning (hysteresis) requires contact angle modulation several degrees beyond a flat meniscus to achieve oil flow in either direction. For tunable color surfaces, this pinning may actually be preferred because various grayscale states (intermediate oil positions) might be selected using pulse width modulated voltage above/below threshold and then maintained with a voltage at threshold. A plot of the maximum change in reflectivity is shown in Fig. 3. As shown in Fig. 3, a large change in reflectance spectra can be achieved. Tunable color performance for this first demonstration is limited by two factors: (1) the unavoidable appearance of red oil at the bottom of the microwell and (2) reflection from the spacing between the microwells. Contrast ratio could be improved by decreasing the aperture size at the

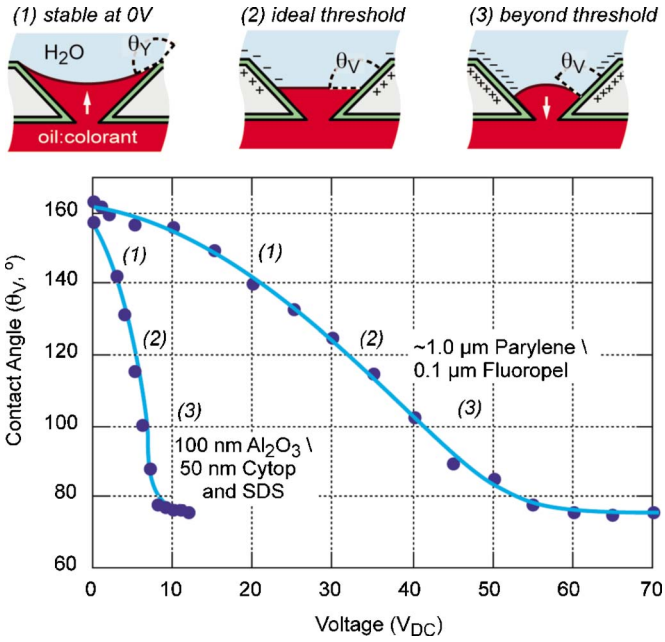


FIG. 2. (Color online) Contact angle vs voltage curves on a planar surface, and diagrams of relation to fluid motion in the electrowetting microwells.

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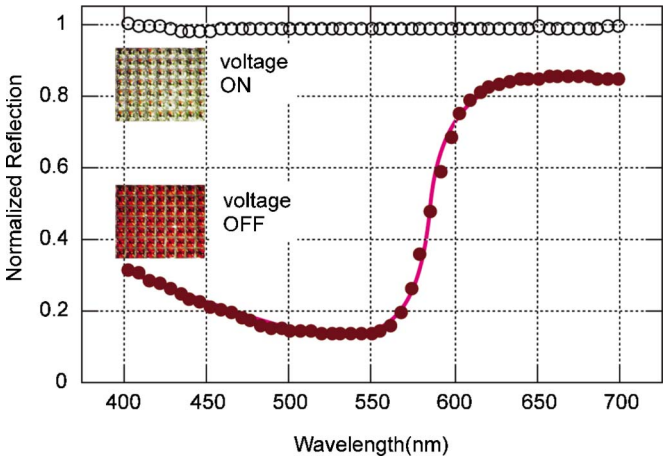


FIG. 3. (Color online) Reflected spectra achieved by placing the device inside a ~50 cm diffuse reflective sphere with a white lamp at the bottom, and recording the reflection signal with a 0.22 numerical aperture optical fiber held above the device. The spectra are recorded for the maximum on and off states of operation, and are normallized to the on state where the oil is driven to the bottom of the microwells.

bottom of the microwell, by placing a nonreflective material behind the device, by more closely spacing microwells, and by using refractive index matched solid and liquid materials to reduce Fresnel reflections from material interfaces.

The thorough reader may have noticed that the microwells using colored water, diagramed in Fig. 1(c), have not yet been discussed. This discussion is judiciously not presented since microwell operation for Fig. 1(c) can be understood by reexamining Eqs. (1) and (2) with the liquid positions reversed. Such microwell arrays using colored water were demonstrated, but were more difficult to operate because (1) they require a smaller electrowetted contact angle and therefore higher voltage to drive fluid flow and (2) the colored water does not achieve a stable energy minimum in the microwell (i.e., the colored water easily recedes past the lower rim of the microwell). The latter difficulty further requires a rounded surface profile at the bottom rim of the microwell to reduce the transitional pressure required to first bring the water into the microwell.[8]

Lastly, possible applications are briefly speculated on and general challenges are presented. One possible application of the electrowetting microwells is electronic paper where white state reflectivity for commercial products[9] is only ~30%–40%. With some optimization, microwell arrays could theoretically provide >80% white state reflectivity and a highly saturated color or black state. For such applications, a preferable substrate might be a microreplicated diffuse white substrate that is coated with a transparent $In_2O_3:SnO_2$ electrical conductor. Considering that electrowetting into the pores of nonwoven polymer textiles has been demonstrated,[10] implementation on polymer substrates is certainly achievable. Other applications worth of mention include microwells with a 45° sidewall slope, and three triangular sidewalls, thus forming a switchable retroreflector.[11] Lastly, if high refractive index oils such as polyphenyl ethers ($n \sim 1.7$) are used in conjunction with water ($n \sim 1.3$), modified microwell structures with widths on the order of a wavelength of light might be utilized to create a new class of switchable or tunable photonic crystals. A common challenge for all of these possible applications is that the microwells require nonplanar fabrication. Therefore, applications requiring control of individual microwells (i.e., pixelation) may be more difficult to produce. Furthermore, as can be seen in Ref. 12 the switching speed and uniformity need be improved.

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[12] See EPAPS Document No. E-APPLAB-92-026812 for supplemental videos of operation for Figs. 1(b) and 1(c). This document can be reached through a direct link in the online article's reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

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