

A full description of a simple and scalable fabrication process for electrowetting displays

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Abstract

Electrowetting displays provide a high white state reflectance of >50% and have attracted substantial world-wide interest, yet are primarily an industrially led effort with few details on preferred materials and fabrication processes. Reported herein is the first complete description of the electrowetting display fabrication process. The description includes materials selection, purification and all fabrication steps from substrate selection to sealing. Challenging materials and fabrication processes include dielectric optimization, fluoropolymer selection, hydrophilic grid patterning, liquid dosing, dye purification and liquid ionic content. The process described herein has produced pixel arrays that were switched at <15 V on active-matrix backplanes, and which have individual sub-pixel areas of $<50 \times 150 \mu\text{m}^2$. The majority of fabrication processes can conform to liquid-crystal style manufacturing equipment, and therefore can be readily adopted by many display practitioners. Also presented are additional tips and techniques, such as controlling the onset of oil film break-up in an electrowetting display. This paper should enable anyone skilled in displays or microfabrication to quickly and successfully set up research and fabrication of electrowetting displays.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electrowetting displays were first reported in 2003 by Hayes and Feenstra at Philips Research Labs [1], who have now led electrowetting display development well into commercialization at their start-up company Liquavista (The Netherlands). In 2005, a second group at the University of Cincinnati reported transmissive and emissive electrowetting display formats [2, 3]. Excluding the quite different approach of 'droplet driven displays' in development at ADT in Germany [4], no other publicly known efforts exist in electrowetting display development. This might be considered surprising, since electrowetting displays provide substantial advantages for displays including video speed [1], >50% white state reflectance [5] and >80% transmissive mode operation [6]. Nearly all scientific journal publications have originated from Philips Research labs or the University of

Cincinnati, which include descriptions of the electro-optic response [7], the effect of dye loading in the oil [8], self-assembled oil dosing [9] and oil film break-up [10]. However, despite these publications, a complete description of the fabrication process used to create an electrowetting display is still lacking. Consequently, reported herein is the first detailed description of the materials, sources, preferred processes and module assembly for electrowetting displays. First, a brief review of electrowetting display operation is provided. Next, the fabrication process for electrowetting displays is described for use on flexible or active matrix substrates. Also, materials selection recommendations are provided. Finally, operation characteristics for completed electrowetting displays will be presented. The goal of this paper is to enable anyone to set up electrowetting display fabrication and testing, and thereby further expand the global research base supporting this new technology.

2. Electrowetting operation

A brief discussion of the principles of electrowetting display operation is first provided.

2.1. Electrowetting basics

In electrowetting displays, an electrostatically induced break-up of a colored oil film is utilized to alter the perceived coloration of a reflective or transmissive pixel. The basic operational principle is electrowetting, as shown in figures 1(a) and (b). An excellent general review of electrowetting science and technology was recently reported by Mugele [11] and a review of electrowetting herein will be brief. The electrowetting effect operates as follows: (1) at zero voltage the three-phase oil/water/dielectric system situates itself at Young's contact angle (θ_Y) and (2) a voltage is applied and a net *horizontal* electromechanical force [12, 13] causes the observed contact angle to reduce to θ_V , according to

$$\cos \theta_V = \cos \theta_Y + \frac{1}{2} \cdot \frac{C \cdot V^2}{\gamma_{AO}}, \quad (1)$$

where C is the capacitance per unit area of the hydrophobic dielectric (F m^{-2}), V is the dc or the ac RMS voltage and γ_{AO} is the interfacial surface tension between the aqueous and oil phases (N m^{-1}). The electrowetting response is analog, and completely reversible with only several degrees of contact angle hysteresis. Numerous materials systems can allow modulation of contact angles from $\sim 180^\circ$ to $\sim 60^\circ$, with a lesser range of contact angle modulation required for an electrowetting display.

2.2. Basic electrowetting pixel operation

As shown in figure 1(c), an electrowetting pixel requires only one additional feature, a hydrophilic grid. The top surface of this hydrophilic grid is always wetted by the aqueous phase, and therefore 'pixelates' the oil into a discrete and arrayed format. The conventional operation of an electrowetting pixel as shown in figures 1(c)–(e) includes two steps and can be described as follows. In the first step, a voltage is applied between the aqueous electrode and an electrode beneath the hydrophobic dielectric. This applied voltage creates an electromechanical force which is primarily vertically oriented (with exception of the effect of the hydrophilic grid). When the voltage is above a certain threshold to overcome surface tension forces, the electromechanical force will break up the oil film. The nature of this break-up is a function of the magnitude of the voltage step, and follows spinodal dewetting theory [14]. A complete analysis of spinodal oil film break-up is provided elsewhere [10]. This first step of breaking up the oil induces a threshold voltage that in poorly designed cases can represent the majority of the required operating voltage. In the second step, once the water contacts the fluoropolymer surface the traditional electrowetting effect begins, involving a *horizontal* electromechanical force [12] and a reduction of the contact angle and therefore the viewable area of the oil droplet. The mathematical relationship between the contact angle and the oil area can be found elsewhere [7]. After

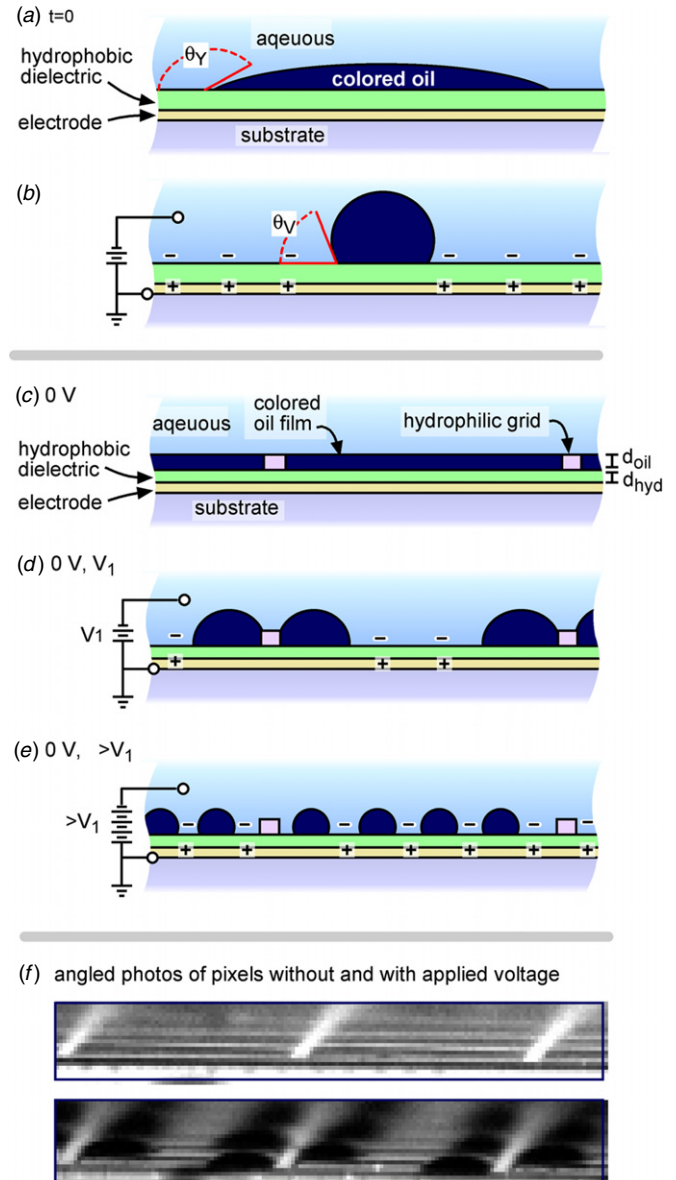


Figure 1. Operating principles for (a) and (b) a basic electrowetting experiment and (c)–(f) a basic electrowetting display pixel. (a)–(e) reprinted with permission from [10]. Copyright 2008 by IOP Publishing Ltd.

voltage is removed, the oil recovers the pixel surface so long as the hydrophobic dielectric is of high quality (smooth, hydrophobic, no charging) and γ_{AO} is suitably high, as will be discussed in a later section.

2.3. Designs for predetermined oil-film break-up

The topic of spinodal dewetting for a flat oil meniscus is presented for completeness of understanding. However, in an ideal embodiment, the oil-film break-up should be made predetermined and independent of voltage. Predetermined oil-film break-up can be achieved in multiple ways: (1) patterning part of the pixel with a hydrophilic feature that starts the dewetting process and generates a single oil droplet [15]; (2) two-step voltage application for single drop formation ($<10\text{--}15 \text{ V}$) [10]; (3) a convex oil meniscus at 0 V , resulting

in one centered drop when voltage is applied [16]; (4) a slightly concave oil meniscus resulting in two drops for a rectangular pixel or possibly four drops for a square pixel; (5) a geometrically non-symmetric hydrophilic grid (discussed in a later section). From an optical contrast point of view, few or a single droplet formation is preferred [10]. A predetermined oil dewetting pattern is also useful to reduce or eliminate the threshold voltage associated with oil-film break-up. The key benefit is not necessarily a lower voltage, as the voltage used to firstly break up the oil film is also secondly used to lessen the water contact angle and reduce the viewable area of the oil. Rather, the key benefit of a predetermined oil-dewetting pattern is a wider set of available gray-scale states. For example, if the threshold voltage is 6 V for oil-film break-up, and only 7 V is needed to achieve 60% transmission or reflection, then many of the lower transmission/reflection pixel states are not accessible without a two-step voltage waveform (one for oil-film break-up, and one for grayscale selection). Again, techniques such as a hydrophilic starting point allow access to all grayscale states with only a single-step voltage.

2.4. Electro-optic response

For both transmissive and reflective mode, the oil is colored with >5–10 wt% of a dye and operates by the principles of optical absorption. Dye selection and purification are critical to pixel performance and will be reviewed in a later section. Transmission or reflection is dependent on the viewable droplet area, and therefore dependent on voltage and contact angle. An example optical transmission curve is shown in figure 2, as adapted from [6]. A video of the pixel array shown in figure 2 is also provided with the online supplementary material for this publication. For transmissive operation, generally all materials except the oil are transparent. Also, as shown in figure 2, for transmissive mode it is beneficial to recycle backlight intensity by integrating a reflector beneath the area of the pixel always covered by colored oil [6]. This simple technique results in transmission (>80%) which is far superior to that achieved by conventional liquid crystal displays. Alternately, for reflective-mode pixels any of the following materials may be made reflective: the solid electrode, the substrate or a film behind the substrate. For maximum reflectance, the reflector should of course be as close as possible to the pixel surface.

3. Microfabrication

The processes reviewed herein represent best practices as independently developed at the University of Cincinnati and Motorola. Other electrowetting groups such as Liquavista have not released details on their fabrication processes or preferred materials. Therefore, it is not possible to determine what alternate fabrication approaches may exist. Nonetheless, the authors will describe herein processes and guidelines that provide robust repeatable results using fabrication equipment available to most of those working in microfabrication or electronic devices. The procedures reviewed herein have been

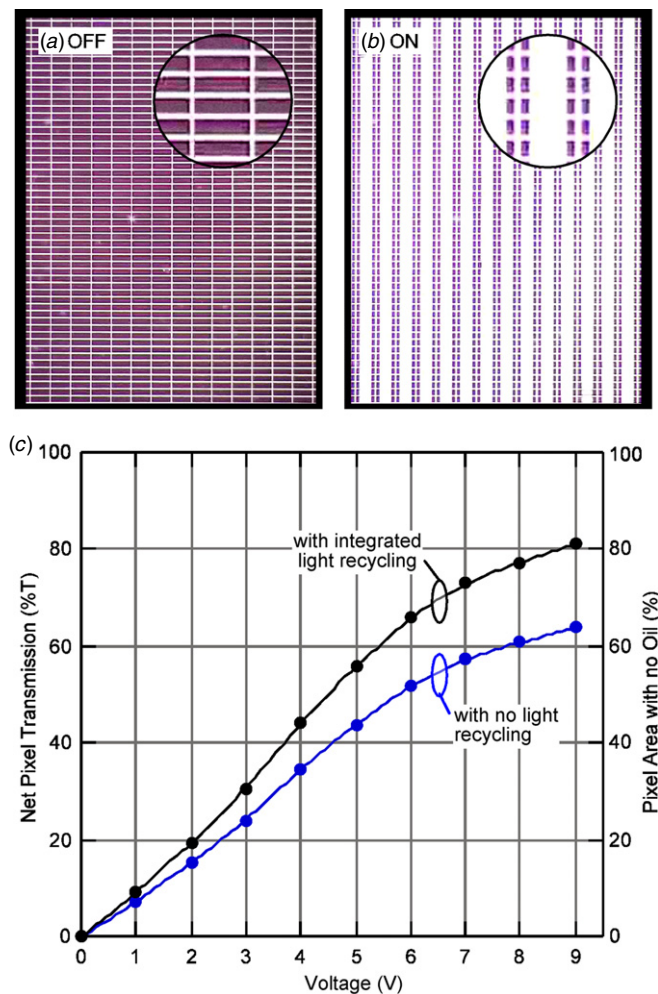


Figure 2. Electrowetting pixel transmission versus applied voltage. Note for (c) that the data include an integrated reflector for backlight recycling, with details available elsewhere [6] (© 2008 IEEE).

shown to produce pixels ranging from 50 μm to 1 mm in size (sufficient to fabricate both smart phone screen pixels and large screen high definition television pixels), and with voltages compatible with active-matrix backplanes (<10 V). Also, the procedures have produced flexible electrowetting display modules, and modules on glass substrates that were driven by an underlying array of industry-provided thin-film transistors. The general steps required for fabrication are shown in figure 3.

3.1. Substrate considerations

Substrate requirements for electrowetting displays are comparable to numerous other display technologies. Firstly, the substrate surface needs only to be smooth enough for thin-film transistors (if desired) or to prevent high field points that would cause premature electrical breakdown of the hydrophobic dielectric. Secondly, the substrate must be able to withstand the processing temperatures required by the fluoropolymer annealing, which range from $\sim 100^\circ\text{C}$ to $\sim 160^\circ\text{C}$ based on fluoropolymer choice (to be reviewed later). Thirdly, the substrates must prevent gas or liquid permeation, with even a few % changes in the volume

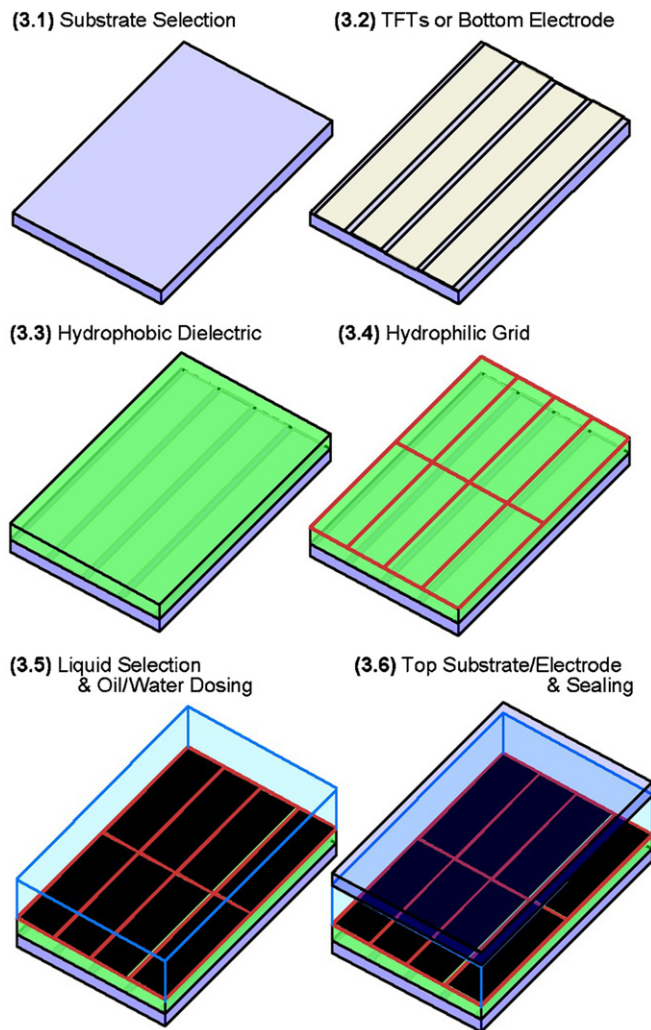


Figure 3. Major fabrication steps for creating an electrowetting display panel.

of the oil being tolerable as long as it is lost uniformly across the panel. Generally, substrates such as PEN, PET or aluminosilicate glass are therefore fully satisfactory for electrowetting displays. For the results described herein one of two substrate types was used: $\sim 100\ \mu\text{m}$ thick PET or polyimide films (Bekaert Specialty Films, LLC), or any of Corning's suite of standard fusion-drawn display glasses. For the processing of flexible substrates at Motorola, a commercially available bonding agent is also used to adhere the flexible substrate to a rigid carrier substrate. Issues which cannot be tolerated are non-bonded areas which leave gas trapped between the flexible substrate and the carrier. Trapped gas would expand substantially during raised temperature ($100\ ^\circ\text{C}$) and/or low pressure processing ($100\ \text{mTorr}$). The rigid carrier substrate allows for proper registration of multiple mask steps. Using this process, Motorola has successfully scaled up from $50\ \text{mm}$ square substrates to $300\ \text{mm}$ flexible rounds. Further notable requirements for flex processing at Motorola include the plasma-enhanced chemical vapor deposition (PECVD) of silicon oxynitride (SiON) at $100\ ^\circ\text{C}$, and backside cooling during plasma processing steps. However, it should be noted finally that creating a simple

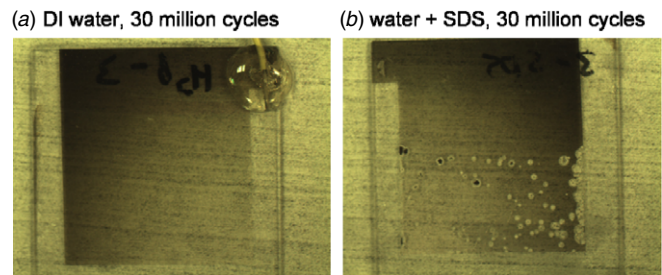


Figure 4. Accelerated aging experiments with 30 million electrowetting cycles using $\text{In}_2\text{O}_3:\text{SnO}_2$ /dielectric/fluoropolymer and (a) DI water, and (b) 1 wt% sodium dodecyl sulfate (SDS) in water.

direct-drive test array requires only one mask step and can be achieved by simply Kapton taping the flexible substrate to a glass carrier.

3.2. Electrodes

Electrodes for electrowetting displays can be common metals, or transparent $\text{In}_2\text{O}_3:\text{SnO}_2$ which may be used in films of ~ 10 to $\sim 100\ \text{nm}$ thickness. For the results reported herein, the lower electrode is always $\sim 50\ \text{nm}$ of sputter-deposited $\text{In}_2\text{O}_3:\text{SnO}_2$ ($\sim 100\ \Omega/\square$). There are two major issues regarding electrode selection. Firstly, electrowetting at low voltages requires electric fields on the order of approximately hundreds of kV cm^{-1} [17]. Patterned electrodes should therefore have the absolute minimal film thickness, or have rounded edges, in order to prevent premature electrical breakdown at the electrode edges. Secondly, the electrode should be somewhat electrochemically resistant to the aqueous solution. This requires careful choice of aqueous content, especially ionic species which can be driven through dielectric defects and which by their ionic nature are inherently reactive. Even the smallest defect in the dielectric can be problematic. For example, as shown in figure 4, a sample that exhibited the undetectable leakage current in the virgin state exhibits no electrochemical aging in deionized (DI) water, but with 1 wt% sodium dodecyl sulfate reveals the location of dielectric pinholes and propagating electrochemical attack of the electrode.

3.3. Hydrophobic dielectric

Although electrowetting can be performed on a single fluoropolymer dielectric such as Teflon AF [17], the two-layer dielectric approach is most often employed because it provides higher capacitance (lower voltage) and potentially greater reliability. This is because stand-alone fluoropolymers inherently do not densify well and can exhibit a porous network that leads to electrical breakdown. Even a porous insulator that works well for solid-state application will not work well in electrowetting because under applied field the aqueous solution is an electrode that can actually *propagate* through a porous network. However, the porous and conductive pathways that plagued a stand-alone thin fluoropolymer are no longer a problem if (1) they terminate against the superior

insulation properties of a lower inorganic dielectric and (2) the pore density is low enough that charge injection into the fluoropolymer does not degrade the electrowetting response to voltage. Therefore, a two-layer hydrophobic dielectric approach was used, consisting of a lower or *insulating* dielectric and an upper *fluoropolymer* dielectric. The two-layer approach also allows a more separate optimization of dielectric and hydrophobic properties, but as will be discussed below, these two properties are never fully decoupled. Another advantage of this approach is similar to that of the multi-layer inorganic/organic hermetic barrier technology developed for OLEDs: a multi-layer dielectric requires direct overlap of individual dielectric defects, such as pinholes, in order to provide an effective path for electrical breakdown or chemical permeability.

Several exemplary *insulating* dielectrics that were demonstrated in this work include Parylene C, Al_2O_3 , AlON, SiN and SiON. For the inorganic dielectrics, low-temperature deposition processes include plasma-enhanced chemical vapor deposition or atomic-layer deposition. Dielectric deposition techniques such as sputtering are more challenging as they result in a greater density of dielectric defects. Example dielectric thicknesses include 2–3 μm for organic Parylene C, and ~ 100 –300 nm for the above-mentioned inorganic dielectrics. Because of the onset of a leakage current for Parylene C thicknesses of <1 –2 μm , it was not possible to obtain a thin and high capacitance layer of Parylene C for low voltage operation. Therefore, for the low-voltage results described herein, the thinner and higher permittivity ($\epsilon_r \sim 6$ –10) inorganic dielectrics were employed with relatively equal success.

It was found that most critical aspect of the hydrophobic dielectric was not the lower *insulating* dielectric, but the upper coating of the hydrophobic *fluoropolymer*. Three leading fluoropolymers were tested, all spin-coated and baked from a fluorosolvent solution, all with a film thickness of ~ 30 –100 nm (if thicker, the fluoropolymers with $\epsilon_r \sim 2$ would severely limit the capacitance). First, Teflon AF was explored, but it exhibited high porosity for the thin films explored herein, and was subject to substantial charge injection which results in poor electrowetting behavior. Asahi Cytop 809M of ~ 50 nm thickness was found to work quite well, consistent with low voltage results reported elsewhere [18]. However, one limitation of Cytop for flexible displays is annealing at ~ 160 –180 $^\circ\text{C}$ for ~ 20 –30 min. The anneal promotes adhesion, densification and improved electrical breakdown field. However, lower temperature annealing at 100 –120 $^\circ\text{C}$ has also been shown to work for electrowetting displays, but repeatability and reliability are still under investigation. For flexible displays, both Motorola and Cincinnati have validated Cytonix Fluoropel 1601 V as a lower temperature alternative. As stated on Cytonix's website, all Cytonix products are Toxic Substances Control Act (TSCA), Restriction of Hazardous Substances (RoHS), Registration, Evaluation and Authorisation of Chemicals (REACH) & Waste Electrical and Electronic Equipment (WEEE) compliant. Fluoropel (PFC 1601 V) in fluorosolvent (PFC 16) can be applied by spin-coating at 2000 rpm for 30 s, baked at

~ 120 $^\circ\text{C}$ for 15 min to form an ~ 50 nm solid film with a surface energy of ~ 16 mN m^{-1} . As will be discussed in the next section, the choice of using Fluoropel does impose additional constraints on the hydrophilic grid processing.

3.4. Hydrophilic grid

The requirements for the hydrophilic grid are as follows: (1) it should be wetted with the aqueous liquid, with Young's contact angle in the presence of oil that is preferably $<120^\circ$; (2) it must not dissolve or degrade over time in the presence of water, oil or light; (3) it is desired between ~ 4 and 12 μm thick and to be photo-patternable such that it can be applied for high fill-factor pixels and high resolutions of ~ 10 μm ; (4) if applied in a solution format, the solution should not foul the fluoropolymer surface; (5) quite challenging, it must adhere to the fluoropolymer with such strength that it survives even a finger-nail scratch test. It has been determined that Microchem SU-8 negative-tone photoresist is an exemplary choice for the hydrophilic grid. Even sealed electrowetting displays constructed at the University of Cincinnati more than 2 years ago with SU-8 grids are still fully operable. The only challenge with SU-8 is the application method, for which two processes have been developed.

The first process is optimized for use on Fluoropel 1601 V. It is not possible to easily spin, spray or dip-coat the SU-8 photoresist onto Fluoropel. A variety of leveling agents were attempted such as Cytonix Corp. FluoroN, which allows the SU-8 to be spin-coated, but the resulting adhesion at the end of processing was extremely poor. Therefore, the Fluoropel surface was first made hydrophilic in a low-power oxygen plasma, and then SU-8 was applied. Specifically, SU-8 2010 (Microchem) was spin-coated at speeds ranging from 2500 rpm to 6000 rpm with resulting SU-8 thicknesses from ~ 12 μm to ~ 4 μm . After a soft bake in a convection oven at 95 $^\circ\text{C}$, the hydrophilic grid pattern was transferred through a photomask, polymerized under 300 mW cm^{-2} exposure ($\lambda = 365$ nm) and developed with SU-8 developer. Finally, a hard bake process was performed in a convection oven at 180 $^\circ\text{C}$ for 30 min. This hard bake cures the SU-8 and recovers the hydrophobicity of the fluoropolymer surface. Electrowetting displays (EWDs) are typically fabricated with cell dimensions ranging from 300×900 μm^2 to 50×150 μm^2 , and SU-8 grid linewidth ranging from ~ 5 to 20 μm . The above process works well for flexible displays where a color-filter array is not used on the top substrate, because no further mask registration or photolithographic steps are required after the grid construction.

The second process is optimized for use on Asahi Cytop fluoropolymer. No additional plasma treatment is required, but a special process sequence is needed. First, the Cytop is spin-coated as previously described, except that it is only soft-baked at ~ 90 $^\circ\text{C}$ for ~ 15 min (no hard bake yet). After soft bake, the Cytop surface energy is not lowered to its minimum value of ~ 20 mN m^{-1} and the surface is not further leveled by an anneal. Next, the SU-8 hydrophilic grid is applied as described above, and adheres well to the unannealed Cytop surface. Finally, the Cytop and SU-8 grid are together hard-baked at ~ 160 $^\circ\text{C}$, resulting in adhesion between the hydrophilic grid

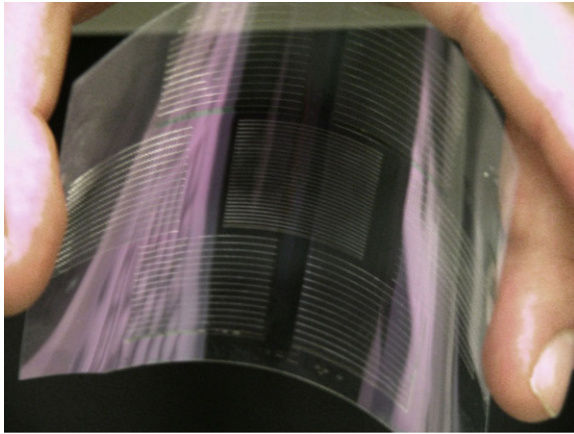


Figure 5. Flexible substrate complete with several electrowetting display test patterns consisting of electrodes, hydrophobic dielectric and hydrophilic grid. Reprinted with permission from [9]. © 2007, American Institute of Physics.

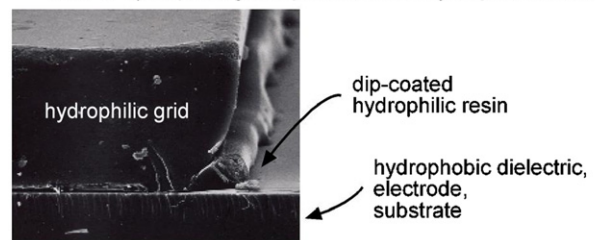
and Cytop that withstands a finger-nail scratch test (figure 5). In short, the SU-8 grid fractures internally before delamination from the fluoropolymer. For flexible displays that require a top color-filter plate, the Cytop should be annealed at ~ 100 – 120 °C for >30 min. However, the Cytop surface energy will be higher than ~ 20 mN m $^{-1}$ and the colored oil in each pixel may need to be a bit thicker if the oil is to recover the Cytop surface at zero voltage.

Several additional process notes should be mentioned. First, oil can merge between two cells during operation in cases where the hydrophilic grid is too narrow, or the applied voltage is too high. These parameters must be engineered appropriately. Second, rectangular grids show more repeatable switching than square-shaped grids as the oil dewetting is more geometrically limited (see the photographs in figure 2(a)). Also, if a single oil droplet is to be generated, Motorola has shown that a trapezoidal grid will cause the oil to dewet regularly in a single direction. Another technique is to dip-coat the substrate at a 45° rotation with hydrophilic resin in a solution (SU-8 or other polymer). The solution does not wet the fluoropolymer, but does situate in the corner of the grid/fluoropolymer. As shown in figure 6, the dip coating causes only one side of the pixel to collect substantial hydrophilic resin. This creates a predetermined wetting pattern. A third issue to address is the loss of hydrophilicity of the SU-8 grid. This has been observed only if the hard bake is performed at >200 °C such that a small amount of fluoropolymer sublimates and redeposits on the hydrophilic grid. A fourth and final issue of discussion is optimized hydrophilic grid thickness. In many designs, the hydrophilic grid determines the height of the oil in the cell [9]. Therefore, the smaller the height of the hydrophilic grid, the lower the operating voltage [9]. However, with current materials, the grid height generally should be >3 – 4 μ m, because at lesser thicknesses the opacity of the oil is insufficient.

3.5. Liquid and dye selection, and preparation

In this section, electrowetting oil, dye and aqueous solutions will be discussed specifically for use in electrowetting displays.

(a) SEM of hydrophilic grid dip-coated with hydrophilic starting point



(b) resulting pixel switching (top-view photographs)

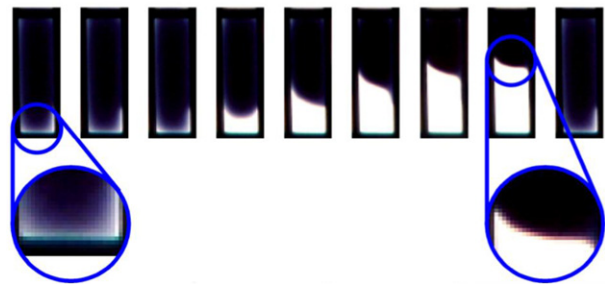


Figure 6. Pixels with a hydrophilic grid that was further dip-coated with a hydrophilic feature at the lower left surface of each pixel. Reproduced with permission from [15] by the Society of Information Display.

In the next section, methods for dosing the liquids will then be presented.

Liquid discussion will first begin with the choice of aqueous liquid. Thus far, the best display results achieved at Cincinnati and Motorola involve use of water without ionic content. Ionic content has been observed to exacerbate dielectric defects such as pinholes, causing electrolysis and/or electrochemical attack of the electrodes (figure 4). Deionized water was experimentally observed to possess the electrical conductivity needed to electrowet pixel arrays at speeds that are not limited by an RC time constant. For DI water, typical interfacial surface tensions with pure oil (no dye) are $\gamma_{AO} \sim 30$ – 50 mN m $^{-1}$. Non-ionic aqueous surfactants can reduce γ_{AO} to lower values of ~ 5 – 20 mN m $^{-1}$, and therefore reduce the operating voltage by as much as $\sim 3\times$ (equation (1)). However, as will be discussed in the next section, no surfactant is needed in the aqueous phase because the high wt% of dye (~ 10 wt%) in the oil acts like a surfactant and lowers γ_{AO} . Regarding extending temperature range (-25 °C to 60 °C), typical non-ionic antifreeze additives, such as propylene glycol, have been added to the aqueous phase and successful electrowetting operation was achieved. Also, it should be noted that the aqueous phase does not require ionic content for density matching of the oil/water, because the pixel size is so small that surface tension dominates, and because unlike electrowetting lenses, vibration-induced oscillation of the oil/water meniscus has little effect on the optical performance.

Regarding oil selection, as reported for the first electrowetting displays [1], dodecane works quite well. Generally the oil should (1) be electrically insulating at >100 kV cm $^{-1}$ and very ‘dry’ like a transformer oil; (2) have low viscosity so as not to compromise switching

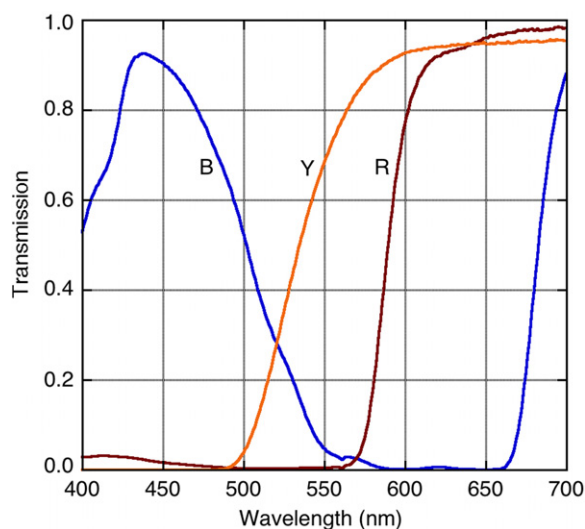


Figure 7. Transmission spectra of the Keystone dye set used to generate blue, yellow, red and mixed together at a B:Y:R ratio by weight of 10:2:4 to create black oil.

speed; (3) be weakly polarizable such that electrowetting relaxation does not occur during low-frequency ac or dc bias. Dodecane possesses all the above characteristics. Experimental measurements further show that tetradecane may be preferred as it allows electrowetting to $\sim 5^\circ$ lower angle than dodecane (i.e. before electrowetting saturation limits the wetting response). Experiments have also been performed with silicone oils or mixtures of silicone oils with alkanes. Generally, the silicone oils exhibit Young's angle close or equal to $\theta_Y \sim 180^\circ$ for a continuous oil film between the aqueous and fluoropolymer phases. Alkanes typically only exhibit Young's angles of $\theta_Y \sim 160\text{--}170^\circ$. Therefore, for the case of a thin hydrophilic grid and oil layer in the pixel ($\sim 3\text{--}4\ \mu\text{m}$), additional silicone oil content can help the oil recover the entire fluoropolymer surface when the voltage is removed.

Dye selection for coloring the oil presents the greatest challenge. At first, conventional solvent dyes such as Blue 36 were explored, but exhibited nowhere near the solubility levels required for creating saturated pixel color. Numerous dyes were sampled and tested until favorable results were finally achieved with Keystone liquid oil dyes. These dyes are highly concentrated, single-phase dyes available in the solution of high flash aromatic solvent. The dye molecules used in these oil dyes are also known as Blue 98, Red 164 and a blend of several yellow dyes for the Keystone liquid oil yellow. The transmission spectra of the blue, red and yellow dyes are provided in figure 7, and are mixed in dodecane or tetradecane at a wt% ratio of B:Y:R of 10:2:4 to achieve a saturated black color. Dye preparation was performed before use, because the dyes are synthesized in the phase (in the carrier solvent) and contain many undesirable impurities. These impurities include (1) carbon and other compounds that are electrically conductive and which reduce the electrical breakdown field of the oil they are dissolved in; (2) highly polarizable molecules that respond to an electric field and cause electrowetting relaxation. The undesirable

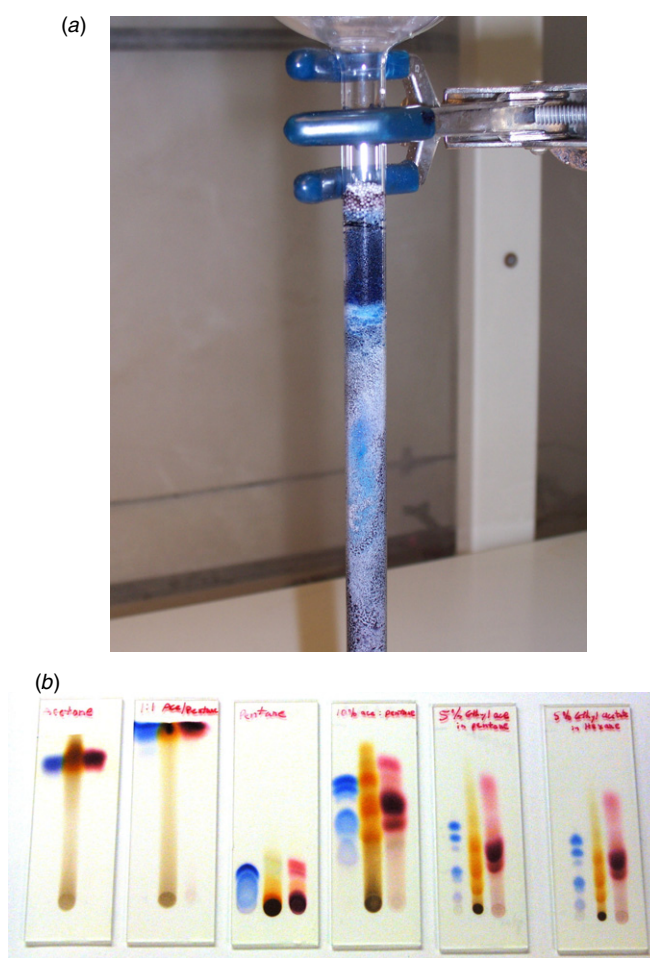


Figure 8. (a) Column and (b) thin layer chromatography for dye purification and characterization. The thin layer slides in (b) are Silica Gel 60 F₂₅₄ with various solvent mixtures.

effect of electrowetting relaxation is observable as follows: when voltage is applied, the electrowetting contact angle is reached first, but then 'relaxes' in $\sim 100\text{ ms}$ to 3 s by several tens of degrees causing the oil to partially recover the pixel surface. To purify, first the dyes were extracted from solvent by heating under vacuum. The remaining solid dye cake was then dissolved in methylene chloride (Fisher Sci., HPLC grade). As shown in figure 8(a), this solution was then subjected to a $3\times$ filtration process through a silica gel column (Whitman, 230–400 mesh, gel replaced for each filtration). The top of the gel column revealed a thin black-colored layer, visibly showing the impurities that were removed. The final purified solution of methylene chloride and dye was then vacuum dried, and the dry dye dissolved into dodecane at $\sim 50^\circ\text{C}$. After this purification, up to 10 wt% dye can be loaded into the oil without degradation of the pixel operation.

A somewhat different but equally effective dye purification process was also developed at Motorola. The dye was dissolved in a solvent mixture used to improve the separation of polar and non-polar components of the dyes. The solvents and mixture ratios were optimized by observing the dye mixture wicking behavior up thin layer chromatography Silica Gel 60 F₂₅₄ slides. As shown in figure 8(b), it was determined that a mixture of 90% hexane

and 10% ethyl acetate separated the polar and non-polar components effectively, and also subdivided the dyes into distinct isomeric bands. Typically, the dyes showed three to six bands with this chemistry. The dye-solvent mixture was then filtered through a silica gel-packed column, and different bands were fractionated off. Once the solvent was removed, majority of the mass of the dye was typically contained in two bands for each color. These dyes were then dissolved in oil.

It should be noted that Liquavista and Mitsubishi Chemical have jointly custom-developed dyes that are likely superior to the Keystone dyes in optical opacity and light fastness. However, these dyes are currently both costly in samples (>\$1000) and require legal restrictions on use. Cincinnati and Motorola have achieved perfectly satisfactory results using the liquid oil dyes from Keystone, and such dyes should enable most anyone to readily explore electrowetting display research and development without need of custom-developed dyes.

A last topic to discuss regarding dyes is their impact on interfacial surface tension. It was observed that the Keystone liquid oil dyes, like dyes previously tested by Philips [8], resulted in γ_{AO} that reduced from $\sim 50 \text{ mN m}^{-1}$ to $\sim 10 \text{ mN m}^{-1}$ as the dye wt% in the oil was increased from 0.1 to $\sim 10 \text{ wt\%}$. According to equation (1), this reduces the operating voltage of the display according to square root of γ_{AO} . The main disadvantage of the reduced γ_{AO} is slower switching speed when the voltage is removed. Also, when the voltage is removed, only the interfacial surface tension forces can cause the oil to recover the pixel surface. Therefore, for a weak γ_{AO} the oil might not recover the entire pixel surface due to contact angle hysteresis. Common causes of contact angle hysteresis of several degrees are a rough fluoropolymer surface, or electrical charging of the fluoropolymer [19].

3.6. Liquid dosing

For liquid dosing, supplying the aqueous phase is not a major challenge. The only issue to be considered for the aqueous phase is degassing such that air bubbles do not appear over time in the sealed display. Any air bubbles cause destruction of the oil dosing in the cells. Proper degassing was achieved by boiling the aqueous phase, by ultrasonication, and preferably by degassing under slight vacuum. Dosing of the oil into pixels is far more challenging. In early work at Cincinnati, EWD pixels were covered by deionized (DI) water and oil was dosed serially using an ultra-precise syringe and x - y micrometer stage. However, this method of oil dosing was time consuming, unstable, inconsistent and difficult to operate, especially for a high-pixel resolution. A new oil dosing method was needed. It has been demonstrated by ITRI that inkjet printing can precisely dose the oil over large arrays [20], followed by covering of the array by water. This approach is effective, but subject to oil evaporation or variation in the dosed volume for small pixels. The simplest approach is self-assembly [9] and has been developed by Cincinnati for use with numerous arrayed electrowetting optic platforms [5]. As shown in figure 9, the electrowetting substrate is slowly lowered through an oil film floating on water. The oil first wets

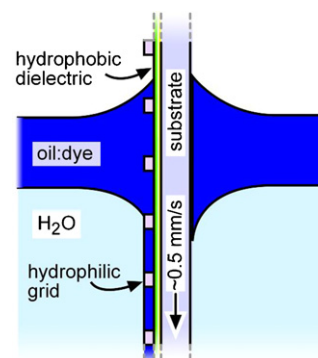


Figure 9. Schematic diagram of self-assembled oil dosing for electrowetting displays. Reprinted with permission from [9]. © 2007, American Institute of Physics.

all features of the EWD display. However, as the substrate is further lowered into the water at $\sim 0.5 \text{ mm s}^{-1}$, the water wets the hydrophilic grid and cuts the oil which remains inside the pixel due to its low surface tension. The self-assembled oil dosing technique has been scaled down to pixels as small as $50 \times 150 \mu\text{m}^2$. It is expected that this oil dosing technique could be scaled down to even much smaller pixel sizes, because it is driven by surface tension which remains homogeneous until the molecular scale is reached. It is important to note that the self-assembled oil films in pixels are geometrically flat and the oil thickness is equal to the grid height with the pixel-to-pixel variation of $<5\%$ of the grid thickness [9].

3.7. Top substrate and sealing

The device now has oil dosed into the pixels, and is next sealed under water. The following sealing process was developed at Motorola. Demonstrated top sealing substrates include ITO/glass and ITO on flexible PEN or PET. Because the aqueous solution is typically non-ionic, resistive and thin, having at least an opaque grid electrode or transparent sheet electrode on the top substrate ensures uniform voltage application to all the pixels. Using a conventional screen printer, a UV-curable bonding/sealing agent was printed onto the border area of the top sealing substrate. To fix the gap at nominally $60 \mu\text{m}$ and provide structural support, spacers are patterned on the top substrate using essentially the same process used to pattern the hydrophilic grid on the EW (bottom) plate. Both the top and bottom substrates have SU-8 outer gaskets on them. The UV-curable material is deposited outside of the outer SU-8 gaskets and adjacent to them. The top and bottom substrates are aligned and pushed together under water. When the plates are brought together, the SU-8 gaskets come together, sealing the water inside and setting the spacing. The UV curable material was then exposed to a UV light (source: Loctite Zeta 7735) which was transferred to the package through a fiber optic immersed in the water. The UV light emitted from the fiber optic was panned around the seal to expose all sides. Curing was completed in less than 30 s to create the final seal. An electrowetting display using UV-curable bonding is shown in figure 10(a), additional UV-epoxy sealed prototypes completed at Cincinnati and at ITRI are shown in figures 10(b) and (c).

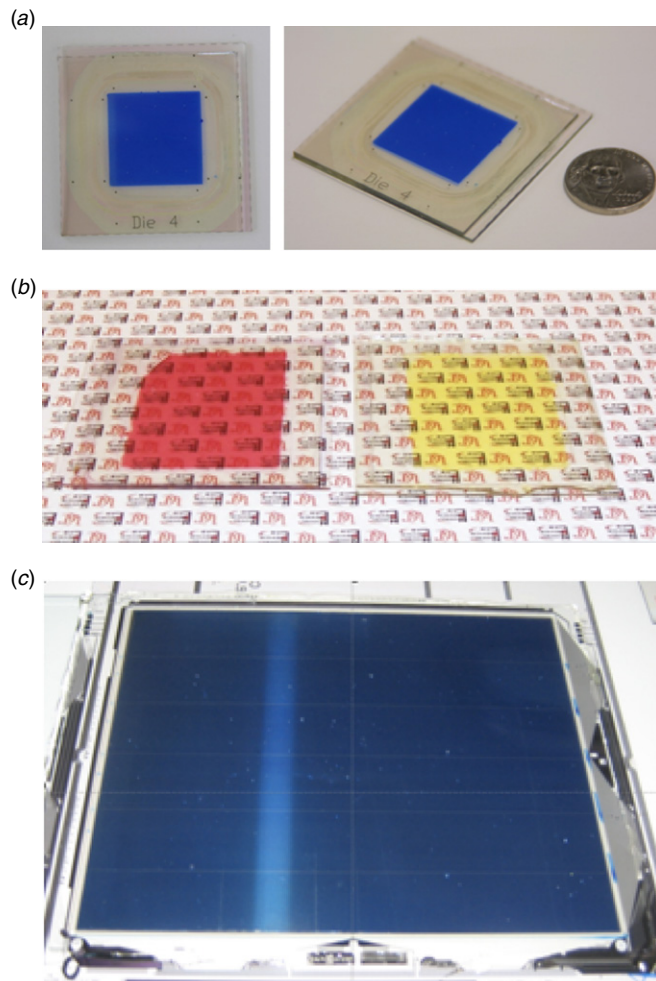


Figure 10. Sealed electrowetting display modules created at (a) Motorola, (b) Cincinnati and (c) ITRI. A nickel coin is shown as a reference in (a), the prototypes in (b) are 2.1" diagonal and the large prototype in (c) is 6" in diagonal and was fabricated using the Gen 2 LCD fabrication facility housed inside ITRI, Taiwan. (c) Reproduced with permission from [20] by the Society of Information Display.

4. Physical fabrication-related results

The electro-optical characteristics of completed modules will be discussed in the next section. In this section, several of the physical-related fabrication results are briefly reviewed. Regarding sealing, completed prototypes were heated to 40 °C for 2 h, and it was demonstrated that packages filled with untreated DI water formed bubbles during the 40 °C step, while packages filled with boiled DI water and vacuum de-aerated water did not. The de-aerated packages were held at still higher temperatures (the maximum test temperature was 70 °C), and no bubbles were observed. At Motorola, more than 100 EW packages fabricated with the o-ring seal method (a process that pre-dated the UV-cure adhesive seal) and the de-aerated water exhibited no bubble formation over time. The oldest packages have been bubble-free for over 300 days at room temperature (corresponding to the date of implementation of de-aerated water use). At Cincinnati, early prototype modules that are >2 years old are likewise fully operable, and free of air bubbles. These results at Cincinnati and Motorola confirm

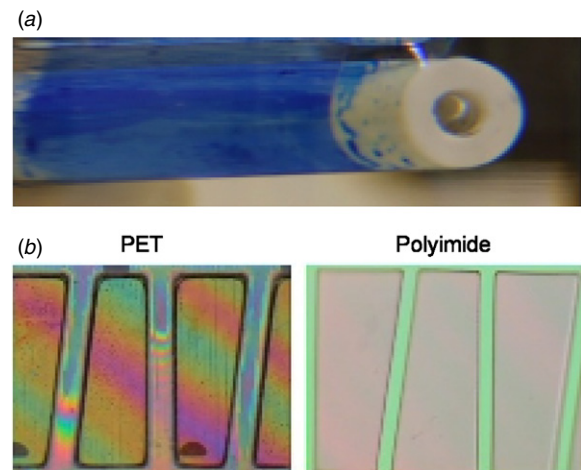


Figure 11. (a) Electrowetting module on a polyimide substrate wrapped around a 6.35 mm diameter tube, and (b) results of pixel rolling 100 cycles around a 10 mm diameter tube for PET versus polyimide substrates.

that most likely there are no major 'shelf-life' issues associated with the fabrication process described herein.

Flexible substrates that have been successfully processed include PET (125 μm thick) and polyimide (100 μm thick) with the layers of SiON, ITO, SiON, fluoropolymer and SU-8. For all flexible substrates the obtained contact angles were equal to those for samples processed on glass at higher temperatures (>160 °C). The flexible substrates exhibited similar display results except when exposed to flexing/rolling tests. Devices on the PET substrates show cracks in ITO and SiON, while the polyimide material shows no cracks in any film layer when flexed. The cracks for the PET film, as shown in figure 11(b), are seen after one flex to a radius of 10 mm. The origins of this cracking are not under further investigation, because devices on polyimide were rolled at a radius of 10 mm greater than 100 times with no cracks appearing. It is also worth noting that for the polyimide substrate, no electrically measured openings in the ITO film could be measured. Of last note regarding physical size is the scalability of the entire fabrication process. It is worth reiterating that the entire electrowetting display fabrication process has been implemented on active matrix backplanes in a Gen2 liquid crystal display (LCD) facility housed in ITRI, Taiwan [20]. This confirms that the process described herein is manufacturable using much of the existing infrastructure and toolsets that are used for large-area flat-panel display production.

5. Electro-optical characteristics

The electro-optical characteristics are now briefly reviewed for display modules fabricated using the process described herein. This section is not intended to provide a comprehensive review of display characteristics, but rather to introduce the reader to achieved results and some general driving considerations. Electrowetting inherently provides an analog electro-optic response, which makes direct-drive segmented displays quite

easy to implement. Active matrix drive is readily compatible except for one challenging factor that will now be described. In the zero-voltage state oil covers the pixel and the capacitance seen by a thin-film transistor is very low (for oil ϵ_r is generally <3 and thickness $>3\text{--}4\text{ }\mu\text{m}$). Consider the example of attempting to set a pixel to white (maximum dewetting of the oil). The response time of the electrowetting pixel is typically on the order of a few milliseconds. However, in a row/column TFT address with 30 Hz refresh and hundreds of rows, the TFT is only charging the electrowetting pixel for tens to hundreds of μs . Even if the full desired voltage is applied while the TFT is 'on' for that short period, as soon as the next row is addressed the TFT is turned 'off'. Because the oil dewets only on the order of $\sim\text{ms}$, the provided charge ($Q = CV$) is still for the case of the pixel predominately covered with oil (low capacitance). Therefore, if the oil continues to dewet after the TFT is turned 'off', the voltage will reduce since C increases but the applied Q remains constant. Due to this reason, it is not conventionally possible to achieve video-rate operation with a single TFT, instead, alternate TFT and drive schemes need to be considered for video-rate operation [21]. Regarding bipolar versus unipolar operation, typically bipolar voltage application is preferred to reduce charging of the fluoropolymer and/or long-term electromigration of ionic species throughout the hydrophobic dielectric.

As shown in figure 12, the effect of pixel geometry on the display operating voltage has already been investigated for modules fabricated at University of Cincinnati [9]. The operation voltage was found to increase with increasing pixel thickness or decreasing pixel width/length. Alternately, one can simply say that the operating voltage increases with increasing pixel aspect ratio. The reason is as follows. For high-aspect-ratio pixels, to move the oil to the designed position, smaller water contact angle is required and thus higher voltage should be applied, which is shown diagrammatically in figure 12(c). This could be resolved if the oil was made thinner, but a practical limit of $\sim 3\text{--}4\text{ }\mu\text{m}$ exists before the oil is no longer saturated in color or where the oil has difficulty recovering the pixel surface in the zero-voltage state. Therefore, when deciding on the pixel grid dimensions (height, width, length), one must understand the tradeoffs between reducing pixel size, color saturation and operating voltage. The above-described constraint typically limits pixel size to $>50\text{ }\mu\text{m}$; otherwise the limit would only be due to photolithography.

Image quality is typically defined by three characteristics: (spatial) uniformity, grayscale and resolution. Resolution has already been addressed in this paper. For an electrowetting display the spatial uniformity depends on the operating behavior of each electrowetting cell and so this behavior is important for practical applications. For a cathode ray tube (CRT), plasma, LCD, micromirror arrays, CCD arrays and other devices comprising arrays of unit cells distributed over an area significantly larger than the unit cell, it is important that each pixel behaves similarly over identical ranges of driver operation. As described earlier, for an EW array, a voltage (specifically, an electric field) applied to an EW cell results in a relative displacement of the colored oil and

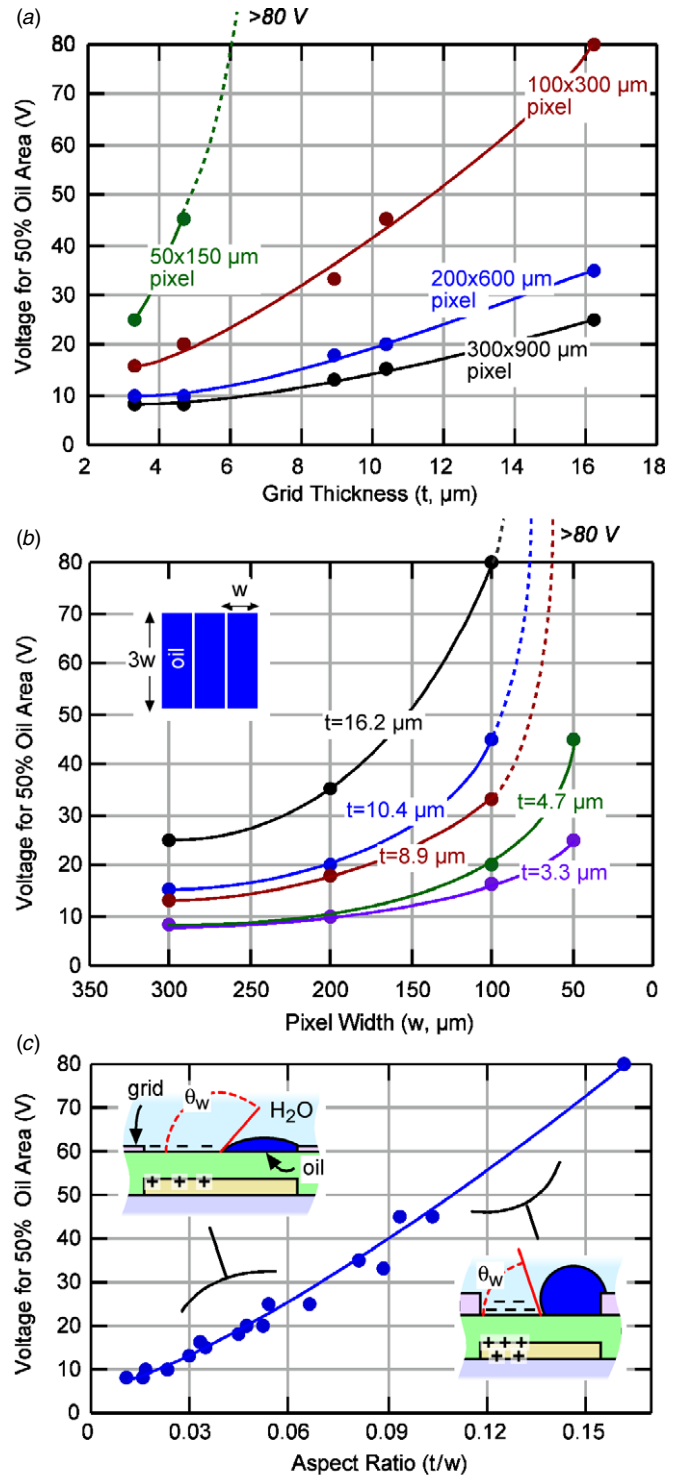


Figure 12. Voltage versus pixel dimensions for electrowetting pixels. Reprinted with permission from [9]. © 2007, American Institute of Physics.

so modulates the transmissive area of the cell. The aim to control this transmissive area is analogous to the desire to control luminance in a CRT or LCD. In the case of an EW display, the per-cell voltage thresholds for both 'off' and 'on' states, within the population of all unit cells, must form a suitably narrow distribution. This ensures that the drive

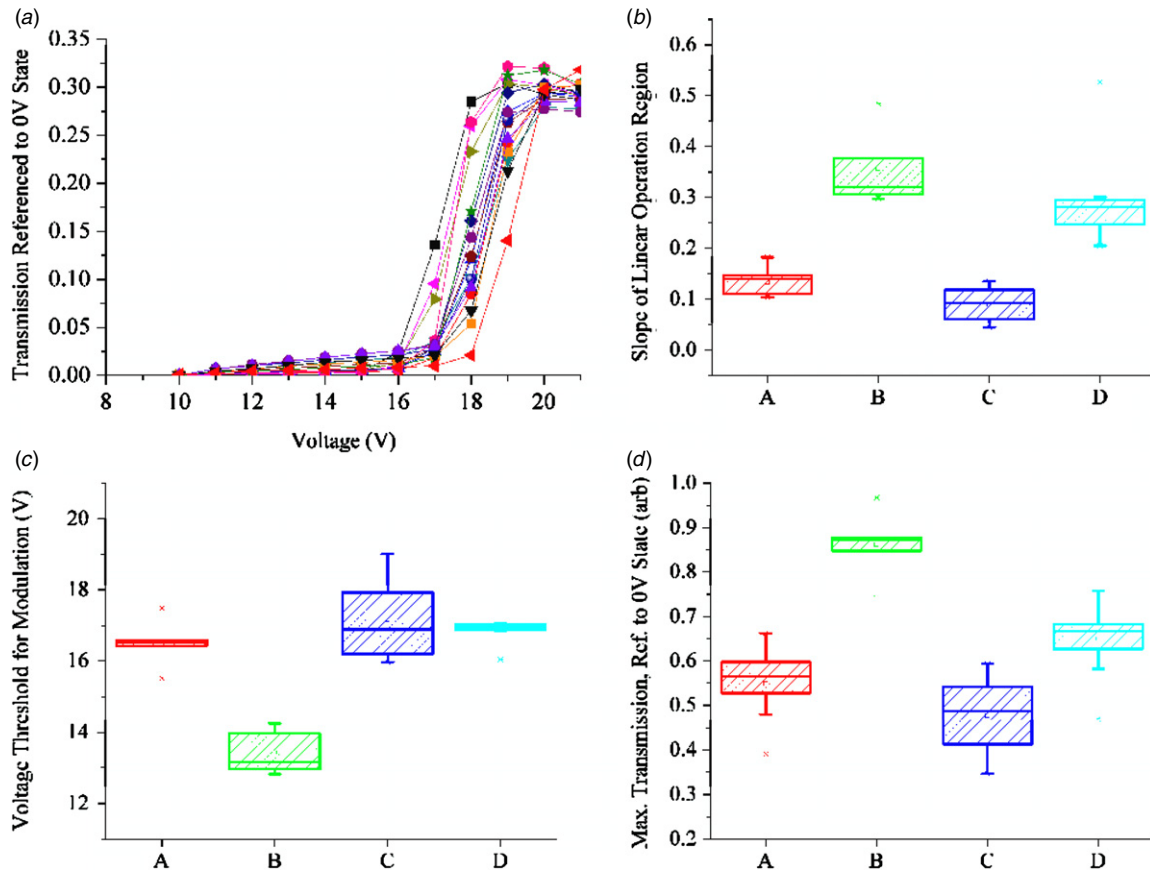


Figure 13. (a) Optical transmission versus voltage curves for an exemplary EW device. Each curve represents one of 16 areas of a 4×4 division of the device surface. Box plots comparing distributions of performance characteristics for four EW devices: (b) slope of the linear operation region, (c) threshold voltage for operation and (d) transmission maximum.

swings between ‘off’ and ‘on’ states are similar for all cells and that no cells require excessive ‘over-driving’. In order to use an analog grayscale approach, the transmission–voltage curves must also be well matched so that, for example, a 25% grayscale value is very consistently 25% across the array. Significant variations produce an effect which is objectionable to the observer. At Motorola, array-level uniformity was characterized by measuring light transmission through the array as a function of the applied voltage. The transmitted light was measured for sections of the module at multiple points across each array tested. A Xe arc lamp (Fiberoptics Technology, Inc., Xenalight) or a halogen lamp (Fostec DCR-II) was used as the light source and was coupled via fiber optic light guide to a light-diffusing pad which was placed beneath the EW array. A matte black plastic sheet with a 4×4 array of apertures was placed over the top of the EW device to define a grid of test areas, each of which could be interrogated independently of adjacent areas. Depending on cell geometry, ~400–600 individual EW cells comprised each measurement area. The transmitted light was detected using a photodiode/transimpedance amplifier IC (Texas Instruments OPT101) with fixturing to ensure registration between the 4×4 grid and the EW array. The uniformity data for four variants of the EW fabrication process are presented in the four graphs in figure 13. Devices A and B are variants of the baseline process which have SiON as the under-dielectric;

however, the thermal processing differs between the two. Device C has Parylene C for the under-dielectric. Device D has SiON, but the ITO beneath the hydrophobic dielectric has been patterned lithographically to enhance control of the colorant displacement. The first graph shows the transmission versus voltage curves for the 16 sites from device D. The remaining graphs compare distributions between four devices, A–D, for each of (b) the slopes of the T – V curve in the linear operation regime, (c) the voltage thresholds for modulation (‘turn-on’ voltage) and (d) the maximum transmission values. In the case of device D, four of the total population of 16 sites measured appear as statistical ‘outliers’, and three of those four are attributable to a processing defect along one edge of the array. The remaining population of 12 exhibits distributions worthy of a high image quality display. Implementation of production-worthy process controls and fabrication on a process line dedicated to EW displays would enable realization of entire arrays with such uniformity.

6. Summary

This paper should enable anyone skilled in displays or microfabrication to quickly and successfully set up research and fabrication of electrowetting displays. No special equipment is required beyond that found in a typical electronic device or display development lab, or which can be acquired

at low cost. Complete process description, from the starting substrate to the sealed module, has been provided. This fabrication knowledge was then further described in terms of the switching behavior of electrowetting pixels. Future work includes advanced aging/reliability testing, generation of high resolution gray scale images and further adaptation to industry standard manufacturing tools. Again, it is the intended purpose of this paper that some of these continued tasks may be pursued by other groups. Furthermore, it is expected that new pixel architectures [22] might be developed which may, or may not, rely on the various operational principles described herein.

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