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Complementary Electrowetting Devices on Plasma-Treated Fluoropolymer Surfaces

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A reversal of the normal two-fluid competitive (water vs oil) electrowetting (nEW) on dielectric has been achieved by plasma irradiation of the normally hydrophobic fluoropolymer followed by thermal annealing. This process first renders the surface hydrophilic and then returns it to its normal hydrophobic properties as measured by water droplet contact and rolling angles. In the *plasma*-irradiated and annealed EW device (pEW), the normal two-fluid EW action is reversed after an initial charging step, with the oil layer being displaced at zero voltage and being returned at high voltage. A possible explanation of this effect is a plasma-induced modification of the fluoropolymer, rendering it more susceptible to charge injection and trapping at high voltage. nEW and pEW devices exhibit complementary EW operation, as verified by oil movement and optical transmission. This method can lead to low-power operation of two-fluid EW devices.

1. Introduction

To reduce power consumption, it is desirable to have electronic devices which display mirror on/off current-voltage ("complementary") characteristics or alternatively which can remain in on and off states without external control ("bistable"). A primary example is the complementary metal oxide semiconductor (CMOS) transistor which dominates semiconductor memory applications. The static power dissipation of CMOS circuits is much lower than that of n- or p-type MOS or bipolar circuits since power is only dissipated during switching.¹ Another important example is the liquid-crystal-based display (LCD), where the liquid crystals themselves may exist in one of two stable orientations and power is only required to change the image.²

Electrowetting (EW), the voltage-induced contact angle change of a liquid droplet^{3,4} on a hydrophobic surface, is an important technology in microfluidics and has been widely used for displays,^{5,6} lenses,^{7,8} laboratory-on-chip devices,^{9,10} and liquid-state transistors.¹¹ In many of these applications, the ability to operate in a complementary or bistable mode would provide significant power savings and would result in greater utility. This paper reports on the use of plasma irradiation of the hydrophobic surface and subsequent annealing to produce complementary EW operation with applied voltage.

While in some EW applications a single fluid is utilized, in many cases one uses the competition between polar liquids (such as water) and nonpolar liquids (such as oils) in contact with each other and with a hydrophobic surface. The surface tension of nonpolar organic oils is lower than that of water, which drives the oil layer to preferentially locate itself between the high surface tension water and the low surface energy hydrophobic insulator. The surface energy relationship between these three materials configures the EW structure and enables the competitive EW of water and oil on the hydrophobic insulator by an applied electric field.

Hydrophobic insulators, such as Teflon AF (DuPont), Fluoropel (Cytonix), and Cytop (Asahi Glass), play a key role in the operation of competitive two-fluid (water and oil) EW devices.¹² Plasma irradiation and subsequent annealing can control¹³ the surface energy of fluoropolymers. The hydrophobic nature of the fluoropolymer insulator makes it difficult to build microstructures using conventional photoresists due to poor adhesion to the low-energy surface. Oxygen plasma has been used to solve this problem by modifying the surface property from hydrophobic to hydrophilic for microfluidic chip bonding^{14,15} and bio research applications.16,17

This paper presents the results of an in-depth investigation into the effect of the plasma irradiation and thermal annealing ("plasma treatment") process on EW properties of the fluoropolymer surface. In particular, the reverse EW effect which results from the plasma treatment is described, and possible mechanisms are discussed.

2. Complementary EW Device Operation

The operation principle of normal EW (nEW) and plasmatreated EW (pEW) devices is illustrated in Figure 1. The basic two-fluid EW device includes conducting (water/electrolyte) and

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Figure 1. Operation of electrowetting (EW) devices with normal process (nEW, left column) and with plasma/anneal process (pEW, right column): (a, b) device schematics under floating (or zero) and negative voltage; (c, d) trend in optical transmission with applied voltage; (e, f) photographs of EW arrays under zero and negative voltage.

insulating (oil) liquids. Opposite oil movement in nEW and pEW devices is obtained by controlling the properties of the hydrophobic insulator using exposure to an oxygen plasma followed by thermal annealing. Fluid motion in the device is governed by the electric field applied to the water droplet through the competitive electrowetting effect. A nonpolar red dye is added to the oil layer for visualization purposes.

The term "structure" is used for experiments that involve only a single fluid (water or electrolyte solution). Structures do not require patterning of the surface. The term "device" is used for competitive EW experiments that involve two fluids. Devices require patterning (see section 3) in order to appropriately control the fluids.

Figure 1a shows cross-section schematics of the nEW device. The device consists of a dielectric-covered transparent bottom electrode on the glass substrate (not shown), a hydrophobic insulator layer (amorphous fluoropolymer), a hydrophilic grid, the two fluids (water and oil), and the top electrode (Au wire). The hydrophilic grid is formed using SU-8 photoresist. For Figure 1a, under either no bias ("floating") or zero bias, the low surface tension oil preferentially covers the low surface energy hydrophobic insulator, forming a thin film that excludes the high surface tension water (or electrolyte solution). The active device area is defined by the SU-8 hydrophilic grid, which confines the oil by strongly attracting the water. When voltage is applied to the water droplet, the resulting field across the hydrophobic insulator effectively increases its surface energy and reduces its hydrophobicity, attracting the polar water molecules to the insulator surface. The water increasingly displaces the oil layer to the side region with increasing bias. Figure 1c shows the optical transmission trend with applied bias for the nEW device. As the bias is increased, the oil layer is pushed to the side region, the exposed hydrophobic area is increased, and the resulting optical transmission is enhanced. Since the applied bias is strongly negative when the transmission is "on", one can say that the nEW device is the liquid equivalent of an enhancement-mode metal oxide semiconductor (MOS) device.

In the pEW device, the fluid motion (Figure 1b) and the optical transmission (Figure 1d) are the reverse of the nEW device. This opposite phenomenon originates from the modified properties of the hydrophobic insulator due to oxygen plasma exposure and subsequent thermal annealing. Since in this case the applied bias acts to decrease the transmission, one can consider the pEW device as the equivalent of a depletion-mode MOS device. It is important to point out that the effect of plasma irradiation and annealing on EW properties is not removed by discharging the surface with a water droplet connected to ground.

Parts e and f of Figure 1 show examples of the oil movement of actual 8-cell EW devices without and with plasma/anneal treatment, respectively. Each cell has an area of $100 \times 300 \,\mu\text{m}^2$ and is defined by a $25 \,\mu\text{m}$ wide hydrophilic grid (SU-8). The nEW device (Figure 1e) reaches maximum EW at -16 V, whereas the pEW device (Figure 1f) obtains maximum EW at 0 V.

3. Device Fabrication

For the characterization of the basic properties of complementary EW, two-fluid circular devices were fabricated with a diameter of 1400 μ m. The hydrophobic insulator and the underlying insulator layers are typically 40 and 100 nm thick, respectively. The bottom electrode consists of a 200 nm indium tin oxide (ITO) layer. A 10 μ m high hydrophilic grid uses epoxy-based negative photoresist (SU-8 2010) to confine a 40 nL oil droplet. Finally, a 3 × 3 mm² hydrophobic grid (not shown in Figure 1) is formed using polyimide to confine a 30 μ L water droplet.

An Al_2O_3 layer was deposited by atomic layer deposition (Cambridge NanoTech) using trimethylaluminum (TMA) and H_2O pulses at 200 °C in nitrogen ambient. The pulse width and separation were 0.015 and 8 s, respectively. The thickness of the deposited Al_2O_3 layer was ~100 nm.

Fluoropel (PFC1601 V, Cytonix Corp.) was used as the hydrophobic insulator. Fluoropel is a copolymer mixture of vinyl, perfluoropolyether, and urethane (with perfluoroalkyl groups) components (Brown, J., private communication). A 1% Fluoropel solution in fluorosolvent was spin-coated at 3000 rpm for 30 s, forming a ~40 nm film. A subsequent anneal at 180 °C for 30 min optimizes the Fluoropel adhesion and reduces the surface energy¹⁸ to 14 dyn/cm.

The hydrophilic grid was formed using an epoxy-based negative photoresist (SU-8 2010, MicroChem Corp.). SU-8 was spincoated at 3500 rpm for 2 min, forming a ~10 μ m film. This photolithographic process includes resist soft baking at 65 and 95 °C for 3 min each, 365 nm UV exposure by i-line mask aligner (EVG 420, Electronic Visions Inc.) with an intensity of ~10 mW/cm² for 14 s, postexposure bake (PEB) at 95 °C for 3 min, and development using SU-8 developer for 40 s, followed by isopropyl alcohol rinse for 10 s. Then, the sample was baked at 120 °C for 10 min to improve the SU-8 adhesion to the hydrophobic insulator. The final element of the EW device is the hydrophobic grid (not shown in Figure 1) necessary to contain the water droplet.

A polyimide-based tape (Dupont Kapton) was used for this purpose.

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For plasma-treated samples, the plasma irradiation was performed in an RIE system (CS-1701, March Instruments) for a few seconds (< 5 s) in oxygen ambient at 125 mTorr (base pressure of 40–60 mTorr) with 30–50 W rf power. The oxygen flow rate was 13–15 sccm. This gentle plasma process changed the Fluoropel surface from hydrophobic to slightly hydrophilic, making it easier to spin-coat SU-8 on it. After UV exposure and development, the active circular device area with a diameter of 1400 μ m was defined. However, at this point, owing to the oxygen plasma irradiation the exposed Fluoropel surface is still slightly hydrophilic, which is not desirable for proper EW operation. The hard baking temperature was increased up to 230 °C for 30 min to regain hydrophobicity. The plasma-treated and annealed devices did not experience SU-8 peeling, while some devices without plasma irradiation showed SU-8 peeling in a couple of weeks.

To operate the two-fluid EW device, typically a 30 μ L droplet of 50 mM KCl aqueous solution was placed on the hydrophobic surface. Then, 40 nL of the alkane hydrocarbon dodecane (C₁₂H₂₆, Acros) with a nonpolar red dye (Keystone Aniline Corp.) was injected using a nanoinjector system (Stoelting Co.). The red dye was purified by column chromatography using silica gel (230-400 mesh, Whatman Inc.) and methylene chloride (CH₂Cl₂) to separate polar impurities incorporated into the dye. These polar impurities hinder oil movement and result in higher voltages being required for EW to occur. Because of their different surface energies, the dodecane (25 dyn/cm) oil naturally locates itself between the hydrophobic surface (Fluoropel, 14 dyn/ cm) and the electrolyte (water,¹⁹ 72 dyn/cm). The oil injection process was monitored by a color CCD camera system (Diagnostic Instruments) for top view and CCD color video camera system (Sony) with TV zoom lens (Navitron) for side view.

4. Results and Discussion

4.1. Effect of Plasma and Subsequent Anneal on Fluoropolymer Surfaces. The effect of oxygen plasma exposure on the surface of the hydrophobic insulator is illustrated in Figure 2. The fluoropolymer surface is naturally hydrophobic (Figure 2a), with water contact angle (WCA) of $\sim 120^{\circ}$. The exposure of a fluoropolymer surface to a gentle oxygen plasma (Figure 2b) results in the defluorination and subsequent oxidation²⁰ of the surface forming carbonyl and hydroxyl groups. The hydrophobicity of the surface is decreased due to the incorporation of the oxygenbearing groups, since oxygen is a major source of hydrophilic property.²¹ At this point (Figure 2c), the surface is slightly hydrophilic, with a WCA $< 90^{\circ}$. To regain the hydrophobicity of the surface for proper EW operation, the irradiated structure is annealed (Figure 2d) at relatively low temperatures (< 250 °C) in air, resulting in a WCA very close to that of the initial structure (Figure 2e). By taking the plasma-oxidized fluoropolymer film above its melting point, the annealing process accelerates the rearrangement^{22,23} of the plasma-treated fluoropolymer surface to minimize the interfacial energy. The lowest surface energy components in the film (trifluoromethyl groups) move from the "bulk" to the top surface since air presents the lowest energy surface interface, while the oxidized molecules move toward the



Figure 2. Effect of plasma irradiation and subsequent thermal annealing on fluoropolymer hydrophobicity and hydrophilicity.



Figure 3. Water contact angle in air vs post-plasma-irradiation anneal temperature. Plasma conditions: 50 W, 2 s; anneal conditions: 30 min, air ambient.

bulk of the film. This results in fresh hydrophobic groups being present on the fluoropolymer surface. It should be pointed out that the process conditions during oxygen plasma irradiation need to be carefully selected in order to achieve the reversible effect. Very small changes in process conditions (such as a few watts of plasma power, 1 or 2 s of exposure time, or a few tenths sccm of oxygen flow rate) are sufficient to result in either no change in Fluoropel surface hydrophobicity or irreversible change to a hydrophilic condition.

4.2. Water Contact Angle of Plasma-Irradiated and Annealed Fluoropolymer Surfaces. The effect of anneals at several temperatures on the WCA in air of the Fluoropel surface of a plasma-irradiated structure is shown in Figure 3 for a $10 \,\mu$ L

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deionized (DI) water droplet. The plasma process was performed with 50 W of rf power for 2 s. The operating pressure and oxygen flow rate were 125 mTorr and 13 sccm. The WCA was measured with a VCA Optima XE (Advanced Surface Technology) system. The initial (preplasma) WCA is 120°. Directly after oxygen plasma exposure, the WCA decreased to 84°. Subjecting the structure to cumulative annealing steps (30 min) of increasing temperature leads to a gradually increasing WCA. After the 180 °C anneal the WCA is completely recovered to the initial value of 120°. A direct (noncumulative) anneal at 180 °C yielded the same WCA. For higher anneal temperatures no further increases in WCA are experienced, but slight improvements in water droplet rolling angle are still achieved. By optimizing the plasma (35 W, 2 s) and anneal (230 °C, 30 min) conditions, the complete recovery of both contact angle (120°) and rolling angle (25°) were achieved.

Figure 4 shows the WCA change and the surface charge density of $5 \mu L$ of DI water droplet on structures with and without plasma treatment as a function of applied voltage. The external bias was applied using a function generator (AFG310, Tektronix) and a voltage amplifier (F10AD, FLC Electronics). Each data point in Figure 4a is the average of advancing (increasing voltage) and receding (decreasing voltage) WCA at the specific bias value. The measured WCA hysteresis is 2.4° for both cases. The solid line is the calculated²⁴ WCA from Young–Lippmann relation which describes the relationship between the WCA (θ) and the applied voltage (V)

$$\cos\theta(V) = \cos\theta_0 + \frac{1}{2\gamma_{LV}}CV^2 \tag{1a}$$

$$C = \frac{\varepsilon_0 \varepsilon_r}{d} \tag{1b}$$

where θ_0 is the WCA at zero bias, C is the capacitance per unit area, d is the insulator thickness, ε_0 is the permittivity in vacuum, ε_r is the relative dielectric constant of the insulator, γ_{LV} is the surface tension of the liquid/vapor interface, and V is the applied voltage to the droplet. The measured WCAs for both cases follow the theoretical curve until saturation occurs. For the unirradiated case, the WCA starts to saturate at approximately ± 20 V, and the saturation angles are $\sim 80^{\circ}$ and 85° under negative and positive bias, respectively. The plasma-treated and annealed structure, although it has the same initial WCA (θ_0) of 120°, starts to saturate at lower voltages of approximately ± 16 V and has higher but symmetric saturation angles (θ_{sat}) of ~94°-95° in both polarities. The reason most commonly attributed to the WCA saturation is charge trapping in or on the insulating layer, with air ionization²⁵ and material deficiencies²⁶ also being considered. In the presence of trapped charge, eq 1 can be rewritten^{27,28} as

$$\cos \theta(V) = \cos \theta_0 + \frac{1}{2\gamma_{LV}}C(V - V_T)^2 \qquad (2a)$$

$$\cos\theta(V) = \cos\theta_0 + \frac{1}{2\gamma_{LV}}\sigma_L(V - V_T)$$
(2b)

$$\sigma_L = \frac{\varepsilon_0 \varepsilon_r}{d} (V - V_T) \tag{2c}$$

where $V_{\rm T}$ is the voltage due to the trapped charge and $\sigma_{\rm L}$ is the surface charge density in the *liquid* at the liquid/solid interface. $V_{\rm T}$ in eq 2 is obtained from the data in Figure 4a



Figure 4. Contact angle (a) in air of a 5μ L of DI water droplet and surface charge density (b) as a function of voltage for unirradiated and plasma treated fluoropolymer surfaces. Insert in (b): moisture condensation pattern at the position where a droplet was previously biased (-20 V for 1 min) on the unirradiated surface.

and is used to calculate $\sigma_{\rm L}$. In the WCA_{sat} region, the effect of the trapped charge is to reduce the increase in surface charge density in the liquid with increases in voltage, resulting in smaller WCA changes (i.e., weaker EW effect). Figure 4b shows the calculated $\sigma_{\rm L}$ of the devices with and without plasma treatment as a function of voltage. For both cases, the surface charge density in the liquid gradually increases as the bias is increased (-16 V < V < 16 V for plasma treated device and -20 V < V < 20 V for normal device) before the onset of WCA saturation. Once the WCA is saturated, $\sigma_{\rm L}$ becomes nearly constant. At $\pm 20 \text{ V}$, the plasma-treated structure shows a smaller *liquid* surface charge density than that of an unirradiated structure by $\sim 0.1 \ \mu\text{C/cm}^2$, which is equivalent to an additional $\sim 0.5 \times 10^{12}$ charges/cm² being trapped in the plasma-treated insulator.

It is interesting to point out that a lower level of saturated *liquid* surface charge density (σ_L) is observed for the plasma-treated insulator than for the no plasma case at both positive and negative bias. The fact that the initial WCA in air for both unirradiated and plasma-treated samples is the same while the saturated surface charge density is different indicates that the plasma treatment itself does not result in the introduction of net permanent charge in the fluoropolymer, but rather that it renders it more accessible to charge trapping during the electrowetting process.²⁹

The insert in Figure 4b is the condensation pattern of humid air at the position where a droplet was previously located for the unirradiated structure. While maintaining the applied bias at -20 V for 1 min, the droplet was removed using a tissue. By blowing humid air on the structure surface, polar water molecules

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Figure 5. Effect of voltage increment on water contact angle in air for (a) unirradiated and (b) plasma-treated fluoropolymer surfaces.

preferentially attached to the area where the droplet had been placed. The condensation pattern is a simple indicator²⁸ of locally charged surface by EW. The plasma-treated device also showed a similar condensation pattern.

Figure 5 shows the effect of voltage increment on θ_{sat} for the same 5 μ L of DI water droplet. For the no plasma structure (Figure 5a), the θ_{sat} levels obtained with 2, 4, and 10 V increments are quite similar. However, for the plasma-treated structure (Figure 5b) the larger voltage increments lead to lower values of θ_{sat} in both positive and negative bias regimes, decreasing from $\sim 94^{\circ} - 95^{\circ}$ for the 2 V increment to $\sim 83^{\circ} - 84^{\circ}$ for the 10 V increment (which is close to the θ_{sat} values of the untreated case). Increasing the voltage increment essentially explores the kinetics of the EW operation,²⁷ since the larger increments lead to stronger EW conditions more quickly than small increments. The operation of both nEW and pEW with the larger voltage increments will result in approximately equal WCA modulation. This is important for the switching operation of complementary liquidstate transistors¹¹ (LiquiFETs) (and other two-fluid EW-based devices), where both devices should have approximately equal switching speed.

A similar kinetic effect on θ_{sat} is obtained by operating the EW structures under ac bias. A comparison of WCA versus voltage for dc and ac bias (at 1 kHz) is shown in Figure 6. A 2 V step was used in increasing the bias levels. These EW experiments utilized a 5 μ L droplet of 0.1 M KCl solution for both the no plasma and plasma-treated structures. For the WCA measured with AC bias the rms values of the voltage are used on the abscissa of the graphs in Figure 6. For both structures, WCA saturation is postponed under ac bias compared to dc bias, with larger WCA modulation being obtained. The effect of using ac bias is more pronounced for the plasma-treated structures. The onset of WCA saturation is



Figure 6. Comparison of water contact angle in air for dc and ac (1 kHz) bias: (a) unirradiated structure; (b) plasma-treated structure. 0.1 M KCl solution.

increased from 16 to 20 V, and the θ_{sat} is decreased from 96° to 86°. A similar effect of AC bias operation was observed²⁷ by Quinn et al., who attributed the decreased θ_{sat} to a reduction of charge injection into the fluoropolymer caused by lag between electric field variation and charge carrier motion. The increased WCA modulation indicates that ac operation of complementary nEW and pEW devices will have an advantage in applications that require higher speed.

4.3. Breakdown Voltage of Unirradiated and Plasma-Treated Structures. The breakdown voltage of the two types of structures was measured to investigate the effect of plasma irradiation and subsequent annealing on the fluoropolymer surface (Figure 7). Droplets of 3 μ L of DI water and 0.1 M KCl solution were placed on both unirradiated and plasma-treated surfaces in air. The purpose of the KCl solution was to electrically "short" the contribution of the droplet to the breakdown voltage and, thus, reveal the breakdown of the dielectric stack (fluoropolymer and insulator layers). The application of external bias to the droplets and the measurement of current-voltage (I-V) characteristics were performed using the HP 4140B pA meter/dc voltage source. Breakdown was defined as the voltage where the current reaches 1 μ A. For the DI water droplet (Figure 7a), the breakdown voltage for the unirradiated structure was 34 V, while for the plasma-treated structure it was slightly higher at 38 V. For the KCl solution droplet (Figure 7b), the breakdown voltage for the unirradiated structure was (as expected) markedly reduced to a value of 15 V. On the other hand, the KCl solution droplet on the plasma-treated structure exhibited a much smaller reduction in breakdown voltage, to only 27 V. This clearly indicates that the dielectric stack in the plasmatreated structures has undergone changes which are not revealed by purely surface measurements, such as contact angle and



Figure 7. Breakdown voltages (at 1 μ A current) in air for unirradiated and plasma-treated fluoropolymer surfaces obtained from I-V characteristics: (a) DI water; (b) 0.1 M KCl solution.

rolling angle. Possible mechanisms for this effect are discussed in section 5.

4.4. Capacitance of Two-Fluid Electrowetting Devices. To further explore the differences and similarities between nEW and pEW devices, the capacitance of the two device types was investigated. The contributions to the overall device capacitance are shown schematically in Figure 8. Two capacitive paths exist between the wire electrode in the water droplet and the ITO electrode: through the oil region and through the water-only region. The areas of the two regions change with voltage, but of course their sum is constant. C_{diel} is the dielectric (Al₂O₃) capacitance, C_{fp} is the fluoropolymer (Fluoropel) capacitance, and C_{oil} is the oil (dodecane) capacitance. C_{total} is the total device capacitance given by

$$C_{total} = C_1 + C_2 \tag{3a}$$

$$\frac{1}{C_1} = \frac{1}{C_{diel1}} + \frac{1}{C_{fp1}} + \frac{1}{C_{oil}}$$
(3b)

$$\frac{1}{C_2} = \frac{1}{C_{diel2}} + \frac{1}{C_{fp2}}$$
 (3c)

For the nEW device at zero bias, the oil covers the entire fluoropolymer region and $C_{\text{total}} = C_1$. As the voltage is increased and the oil is displaced, the "white" (oil-less) area of the device increases and C_{total} is the sum of the capacitances through the remaining oil-covered and the water-covered regions, as shown in Figure 8. The reverse trend occurs in the operation of the pEW device, with the maximum white area occurring at zero bias and decreasing with increasing voltage. The capacitance of the structure will be different for nEW and pEW devices biased at the same voltage but should be similar for devices with the same white area.

An HP 4275A multifrequency LCR meter equipped with HP 16023B bias controller was utilized to measure the capacitance.



Figure 8. Schematic diagram indicating capacitive components in two-fluid EW device and capacitance equivalent circuit model.



Figure 9. Capacitance vs frequency at zero bias for normal and plasma-treated EW devices. 50 mM KCl solution; 50 mV ac voltage; no oil.

To obtain accurate measurements, the LCR meter was calibrated to remove unwanted capacitances from cables and probes. Figure 9 shows the capacitance of 30 μ L droplets of 50 mM KCl solution on the surface of both plasma-treated and untreated devices as a function of frequency from 10 kHz to 10 MHz. In these measurements, the absence of oil reduces the capacitance equivalent circuit to the series combination of $C_{\rm fp}$ and $C_{\rm diel}$. At 10 kHz, the capacitances of the plasma-treated and untreated devices were 480 and 435 pF, respectively. A $\sim 10\%$ difference in capacitance between the two devices was evident up to a frequency of ~ 100 kHz. The higher capacitance of the plasmatreated device could be the result of an increased dielectric constant and/or a denser fluoropolymer layer upon solidification after melting during the annealing process. Both capacitance curves significantly decreased at frequencies >100 kHz. This is due to the fact that at a frequency below a certain critical value water (and electrolyte solutions) behaves as a conductor. At frequencies beyond critical values the water molecules and electrolyte ions are no longer able to follow the electric field, and the water droplet behaves as an insulator.³⁰ Because of the thickness of the water layer, the capacitance of the water droplet is quite low in spite of the very high dielectric constant. This leads to the drastic decrease in the total capacitance of the device since the small water capacitance is in series with the capacitance of the fluoropolymer and dielectric insulator.

The capacitance of the two-fluid nEW and pEW devices was measured as a function of applied bias. The ac frequency was 10 kHz, and an ac signal of 50 mV was added to the dc voltage and applied to a 30 μ L droplet of 50 mM KCl solution. The complementary nature of the nEW and pEW devices is evident in their capacitance vs voltage characteristics plotted in

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Figure 10. Capacitance (10 kHz) during operation of nEW and pEW devices in oil: (a) capacitance vs applied voltage; (b) capacitance at various voltage induced device white areas. 50 mM KCl solution.

| Table 1. | Properties | of Materials | Used in | EW | Structures |
|----------|------------|--------------|---------|----|------------|
|----------|------------|--------------|---------|----|------------|

| material | relative dielectric constant | layer thickness (nm) | capacitance/ area (F/cm ²) |
|--------------------------------|------------------------------|-------------------------|---|
| Al ₂ O ₃ | 7.6 | 100 | 6.73×10^{-8} |
| Fluoropel | 2 | 40 | 4.43×10^{-8} |
| dodecane | 2 | 10000 | 1.77×10^{-10} |

Figure 10a. The capacitance of the device is a function of its geometry, oil/water location (controlled by the applied voltage), dielectric properties of the materials, and trapped charge (if any). For the nEW case, the capacitance at zero bias is quite low, as the oil layer covers the entire area. When the voltage is increased, the capacitance increases as the water displaces the oil layer. For the pEW device, the capacitance is largest at zero bias, where the oil displacement is maximum. As the voltage is increased, the reverse EW effect results in oil spreading and a reduction in capacitance. The mechanism for the reverse EW effect is discussed in section 5.

In Figure 10b the capacitance is plotted as a function of exposed white area resulting from voltage-induced oil displacement. Since nEW and pEW devices operate in complementary fashion, the voltage required to obtain a certain white area (i.e., oil displacement) is not the same. The dotted line in Figure 10b contains theoretical capacitance values calculated from eq 3. The relative dielectric constants, film thickness, and capacitance per unit area for dodecane, Fluoropel, and Al₂O₃ are given Table 1. The area of the device is 1.54×10^{-2} cm² (1400 μ m diameter). As seen in Figure 10b, the measured capacitances are quite close to the calculated values, which indicates that the simple model shown in Figure 8 is a reasonable representation of the device operation. This implies that parasitic capacitances and fringing



Figure 11. Wetting properties of DI water droplets in oil (dodecane) as a function of voltage for unirradiated and plasmatreated fluoropolymer surfaces: (a) water contact angle (WCA); (b) water contact line (WCL).

field effects are not a significant factor. The capacitance of the pEW device is slightly higher than that of the nEW device for small white area fractions. This is similar to what was observed for oil-less EW devices at the same frequency (10 kHz), as shown in Figure 9.

4.5. Water Contact Angle in Two-Fluid Electrowetting Structures. To further investigate the effect of plasma irradiation and annealing on the fluoropolymer surface, the wetting properties of DI water droplets in oil ambient were measured as a function of applied voltage. The two types of structures were immersed in an oil (dodecane) bath, and $3 \mu L$ of DI water droplets was placed on the surface. The measured WCA vs voltage is shown in Figure 11a. For the unirradiated structure, the initial WCA in dodecane was 168°, which is much higher than the initial CA (120°, Figure 4) in air ambient. The WCA started to saturate at 20 V (solid square in Figure 11a), and the saturation WCA was $\sim 60^{\circ}$, which is much smaller than the saturation WCA ($\sim 86^{\circ}$, Figure 4) in air ambient. For the plasma-treated structure, the initial WCA (solid triangle in Figure 11a) was identical to that of the unirradiated structure. However, the DI water droplet became spatially unstable ("runaway") at ~12 to 16 V, before the WCA saturation was reached. This phenomenon only occurred for the plasma-treated structure in oil ambient and was observed every time the experiment was performed. To prevent the droplet from running away, 5 wt % of hydrogel (Sigma-Aldrich) was coated at the end of the top electrode (Au wire in this case) to provide a retention force on the droplet. The solid triangles in Figure 11a represent this result. The photographs included in Figure 11a illustrate this phenomenon. However, even with the hydrogelcoated electrode the DI water droplet still ran away after 16 V, as shown in Figure 11a.



Figure 12. Oil coverage vs voltage for two-fluid pEW and nEW devices: (a) DI water + dodecane oil (dye); (b) DI water + dodecane oil (no dye).

The water contact line (WCL) dimensions corresponding to the WCA data are shown in Figure 11b. The WCL of DI H₂O droplets in air shows only minor differences between the normal (unirradiated) and plasma-treated structures. For oil ambient, the WCL of normal structures at low applied voltage is much lower than for air ambient, while the reverse is the case at high voltages. This is consistent with the corresponding WCA measurements. Interestingly, for the plasma-treated structures, the droplet runaway phenomenon occurred when the WCL reached a value of ~ 2 mm.

While the wetting properties measured with water droplets in air seem to be very similar for unirradiated and plasma-treated structures, the properties measured in oil ambient do indicate some differences. Interestingly, the zero bias WCL dimensions are nearly the same for both structures, and differences (including runaway) reveal themselves only at higher voltages. This situation has some similarity to the breakdown voltage situation (Figure 7), where higher voltages are applied to the water droplet and clear differences are observed between the unirradiated and plasmatreated structures. The mechanisms underlying the runaway phenomenon are discussed in section 5.

4.6. Oil Coverage and Optical Transmission of Two-Fluid EW Devices. Oil coverage as a function of voltage for the two-fluid nEW and pEW devices is shown in Figure 12. In Figure 12a, the nEW device at zero bias has 100% oil coverage. Electrowetting in the nEW device starts at -4 V, and the area covered by oil decreases up to 20% of the total device area as the bias is gradually increased to -16 V. When the bias is then decreased to 0 V, the displaced oil returns and covers the entire device area again (100% coverage). The pEW device shows the opposite EW action. Initially, at zero bias pEW also has 100% oil coverage. During the initial increase in voltage, EW action is not observed up to -20 V, and oil still covers the entire device. When the bias is decreased from -20 to -8 V, EW begins and the oil displacement is enhanced with decreasing bias and reaches a



Figure 13. Optical transmission (measured at 532 nm) through two-fluid nEW and pEW devices as a function of applied voltage.

maximum at 0 V with 25% oil coverage, resulting in the "reverse" EW phenomenon. To remove the possibility that this effect could be related to the dye incorporated into the oil for enhancing the oil—water contrast, the same measurements were performed with plain dodecane oil. As shown in Figure 12b, the same trends were observed for both nEW and pEW devices as in Figure 12a, which indicates that the presence of the dye in the oil is not the cause for the reverse EW effect. The possibility of charge injection from the water layer was also investigated by replacing the pure DI water droplet with a 50 wt % water/glycerol solution. The reverse EW action was observed in this case as well.

The effect of reverse EW on optical transmission through the EW device was investigated using a 532 nm laser (PGL-III-532-A, Changchun New Industries Optoelectronics Tech.). The laser output power is decreased to 15 μ W by an attenuator and is incident on the device through the glass substrate. The transmitted light is detected by a fiber-optic spectrometer (SD2000, Ocean Optics) which is positioned just above the water droplet. Figure 13 shows the optical transmission of two-fluid nEW and pEW devices. For the nEW device, the optical transmission starts to increase right after -4 V owing to the onset of EW and gradually increases up to ~80% at -14 V as the exposed hydrophobic surface area is increased due to the displaced oil. In contrast, the pEW device reaches a maximum transmission of ~70% at 0 V and 0% transmission at -18 V due to the reverse EW effect.

5. Discussion

Before discussing the mechanisms for the observed phenomena, it is important to reiterate that the process of plasma treatment did not result in major differences in *single* fluid (water) EW. The voltage reversed effect was only observed for *two-fluid* EW operation, where both water and oil were present.

The modification produced by the plasma treatment on the fluoropolymer/insulator structure and the mechanisms for the related electrowetting properties can be explained by charge injection and trapping. Under one set of conditions (in air and at relatively low voltages) the plasma-treated and untreated surfaces produce nearly identical properties (WCA and rolling angle). On the other hand, in oil ambient and at higher voltages the two surfaces exhibit significantly different characteristics.

Since the charge that produces these changes is not on the fluoropolymer surface (or its effect would be evident under most circumstances), the modification must occur subsurface, either in the bulk of the two insulators or at the interface between the two. The Fluoropel layer is only 40 nm thick and, therefore, does not Article



Figure 14. Model for charge trapping effects on electrowetting in plasma-treated fluoropolymer structures: (a) breakdown voltage in air; (b) droplet runaway in oil.

provide much material for a "bulk" effect. The Al₂O₃ layer is thicker (~100 nm), but the material is quite a robust inorganic dielectric. It is, therefore, probable that the effect resides close to the interface between the two materials, where the plasma irradiation has caused a chemical modification that is not reversed by the annealing process. It is likely that the annealing process, which actually melts the fluoropolymer, results in the incorporation of polar groups (produced by the plasma exposure) previously located on the film surface. This could result in a more polar and more polarizable material, which in turn would result in a higher dielectric constant (explaining the higher capacitance) and a stronger attractive force for trapping injected charge. Charge trapping in the hydrophobic insulator is known to occur at high applied voltage.^{28,31}

One case where the two structures produced a clear difference in air ambient is in breakdown voltage (section 4.3, Figure 7). As voltage is applied to the plasma-treated structure, charge is injected into the insulator stack and is trapped locally. As illustrated in the simple model in Figure 14a, the accumulated trapped charge then counters the charge introduced into the droplet by the external bias, resulting in a smaller effective voltage across the insulator. This, in turn, results in a larger external voltage being required to achieve the breakdown field of the insulator stack.

Charge trapping can also explain the droplet runaway phenomenon described in section 4.5 (Figure 11). As voltage is applied (and increased) to the droplet, an increasing amount of charge is injected and trapped in the insulator stack. As trapped charge builds up, it will eventually reach a point where it provides a sufficient repelling force on the like charges in the droplet to cause the droplet to move. This mechanism is illustrated in the simple model of Figure 14b. The runaway phenomenon was only observed for water droplets in oil ambient. The reason for its absence in air ambient is probably related to the difference in contact line dimensions in the two ambients. The smaller contact Kim and Steckl



Figure 15. Model for reverse two-fluid EW effect based on charge trapping effect: (a) nEW: zero bias; (b) nEW: high bias; (c) pEW: zero bias; (d) pEW: high bias.

line in the case of oil ambient restricts charge injection into a smaller region, increasing the trapped charge density. In turn, this results in a larger local electric field between the trapped charge and the charge in the droplet, forcing the lateral movement of the droplet. While trapped charge is clearly an important contribution to this effect, other factors may also come into play: the smaller contact line and a thin oil layer³² trapped between the droplet and the fluoropolymer layer reduce the friction between the droplet and the surface enabling lateral motion, while the higher viscosity of the oil impedes motion.

Finally, the reverse EW effect in device structures can be also be explained based on charge injection and trapping. As shown in Figure 15, in the normal device (nEW) the absence of applied bias results in a zero field across the dielectric stack and, hence, a continuous oil layer between the water and the insulator. The application of an external voltage (Figure 15b) results in the presence of a high field in the nEW device and the displacement of the oil layer by water. The opposite situation occurs for the plasma-treated device (pEW). In this case, the initial precharging of the pEW device at high voltage results in the presence of trapped charge in the insulator stack. Then, at zero applied voltage a high field is present across the fluoropolymer-water interface due to the trapped charge, leading to the displacement of the oil layer (Figure 15c). Subsequently, as the voltage is increased (with negative polarity in the droplet), the positive charges in the droplet are drained, but no negative charges are introduced due to the repelling force of the trapped charge, resulting in a zero field condition across the fluoropolymer-water interface and the displacement of the water by the oil layer (Figure 15d).

The need for precharging of the structure to exhibit the reverse EW effect is also seen in the contact line measurements of Figure 11. In that case, droplet runaway at relatively low voltage prevented the precharging of the surface, and hence, only the normal EW effect could be observed.

In summary, the most probable explanation for the reversed EW effect has to do with charge injection and trapping in the fluoropolymer insulator layer or at the fluoropolymer/insulator interface. This hypothesis is supported by several observations from the plasma-treated versus the unirradiated structures and devices: (a) a higher level of charge injection in the WCA saturation region in air ambient; (b) a higher capacitance; (c)

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Kim and Steckl

higher breakdown voltage, especially when using KCl solution droplets which emphasize the properties of the fluoropolymer/ dielectric insulator stack; (d) runaway phenomenon at higher voltages for droplet in oil ambient; (e) last, but not least, the application of high voltage to initiate the EW reversal in plasmatreated device structures.

On the basis of all the evidence summarized above, it is clear that this effect is observed in conjunction with the application of high voltage, which results in charge injection and trapping leading to modification of the electrical (including electrowetting) properties of the structure. Future investigation of the reverse EW effect will address the effect of using other fluoropolymers (such as Teflon AF, Cytop), other inorganic insulators (such as silicon dioxide or nitride), and bias methods (such as ac voltage).

6. Summary and Conclusions

In summary, the complementary electrowetting operation using normal *two-fluid* EW device and plasma-treated EW device has been reported. The oxygen plasma process improves adhesion of the hydrophobic fluoropolymer to the hydrophilic grid. Subsequent thermal annealing completely recovers the fluoropolymer hydrophobicity, verified by contact angle and rolling angle measurements. However, the plasma-treated device exhibits unexpected voltage-reversed EW characteristics: oil displacement with low voltage and its return at high voltage. Oil movement and optical transmission experiments support the complementary EW operation of two-fluid nEW and pEW devices. It is important to note that the reverse EW effect has been replicated every time that the plasma treatment was utilized in device fabrication. The observed effects are consistent with the injection and trapping of charge in the insulator stack of the device. The complementary EW technology reported here can lead to low-power operation of EW-based systems.

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