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Evaluation of repeated electrowetting on three different fluoropolymer top coatings

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Abstract
Degradation of the electrowetting effect by a repeated actuation is evaluated over an extended period (200 min) on electrowetting-on-dielectric (EWOD) samples for three popular fluoropolymer top coatings: Teflon, FluoroPel and Cytop. A conductive liquid droplet is tested in an air environment at Electrowetting number $Ew \cong 0.34$. A pulse train (6 sec period and 50% duty cycle) of three different voltage types is used for the actuation: positive DC, negative DC and 1 kHz AC. For the DC actuations, electrowetting degrades gradually on Cytop but significantly faster on Teflon and FluoroPel under the tested conditions. For the AC actuation, electrowetting degrades gradually on all three materials in a similar fashion.

1. Introduction

Electrowetting has become a widely popular mechanism for handling liquid droplets in sub-millimeter scale [1-3]. Practiced most commonly as electrowetting-on-dielectric (EWOD) [2], the electrowetting actuation has been adopted for many applications, such as displays [4,5], optics [6], and lab-on-a-chip [7-9]. While the advances in applications have been exponential and fundamental understanding has grown [10], there still remain a few outstanding issues for EWOD, such as: (1) leakage current through the thin dielectric, (2) degradation of the electrowetting effect for extended actuation, and (3) contact-angle saturation at high voltage. While the first issue has been dealt with to a degree by any developers and also made a significant progress recently [11], the other two have not seen promising solutions yet. Since the degradation is unavoidable, currently most EWOD devices simply avoid actuating the same spots for long periods (e.g., more than several seconds). Although no solution has been proposed for the second issue, the cause of the degradation is widely understood as charge trapping. For example, supported by EWOD experiments of a liquid droplet on oil-impregnated surface in air, Verheijen and Prins [12] explained the influence of trapped charges and suggested dielectric charging models. Tested with a water droplet in oil, later the results of Berry et al. [13] showed the degradation worsening when the applied voltage exceeded the threshold voltage of the dielectric materials. Although fluoropolymer materials are widely utilized as a topcoat for their hydrophobicity, low contact-angle hysteresis and convenience of coating, most EWOD devices include an additional dielectric layer as the main dielectric below the hydrophobic layer. In this work, we focus on the hydrophobic topcoat.

The contact-angle reduction by an applied electric potential, i.e., the electrowetting effect, can be expressed by the following electrowetting equation for EWOD configuration:

$$\cos\theta - \cos\theta_0 = Ew = \frac{\varepsilon_o \varepsilon_r}{2d\gamma} V^2 \quad (1)$$

Here, the electrowetting effect is quantified as the non-dimensional Electrowetting number *Ew*, determined by the dielectric constant ε_r and thickness d of the dielectric layer, the interfacial tension γ between the liquid and the immiscible surrounding fluid and the applied potential *V* [1,10,14]. The contact angles θ_0 is Young's angle, the natural contact angle of the hydrophobic top coating without the applied voltage. While the above equation is quite reliable, it is invalid if the voltage applied is above the saturation value or the dielectric layer has been electrically charged. Thus, we can assess the condition of the dielectric layer by observing contact-angle reduction and comparing it with the initial value. In this report, we define the voltage applied during actuation (= 30 V) and the voltage applied after one actuation cycle (= 0 V) as V_{on} and V_{off} respectively. Since the contact angles depend on the number of actuation cycles (N), we use $\theta_{V_{on}}(N)$ and $\theta_{V_{off}}(N)$ - the contact angle during and after the actuation cycle N, respectively. Also, we introduce the contact-angle reduction at actuation cycle N as:

$$\Delta\theta(N) = \theta_{V_{off}}(N) - \theta_{V_{on}}(N) \quad (2)$$

The goal of this work is to provide a useful reference data of practical importance about the top hydrophobic coating in terms of the electrowetting degradation over repeated actuations. There are three commercial fluoropolymers commonly used today for the hydrophobic top coatings of EWOD devices: Teflon AF 1600, FluoroPel 1601V and Cytop CTL-809M. Another noteworthy hydrophobic layer SiOC [15] is not tested here. To design more reliable devices, it would be useful to comparatively evaluate the susceptibility of these common materials to degradation. In this work, we investigate the performance over time by monitoring contact angles of a conductive liquid droplet in an air environment over 2000 cycles (200 min) of periodic actuation at $Ew \cong 0.34$. Because it requires higher voltages to actuate the droplets in air than in oil, the addressed issue of EWOD degradation is especially important for the air environment.

2. Methods

2.1. Fabrication

A highly doped silicon wafer (resistivity less than 0.0015 Ohm-cm) was thermally oxidized to passivate its surface with silicon dioxide. Measured to be 560-570 nm, this silicon dioxide serves as the main dielectric layer of the EWOD configuration in this work. After removing the oxide on the backside of the wafer by a buffered oxide etcher, a hydrophobic polymer solution (0.78% Teflon AF 1600 from DuPont, 1% FluoroPel 1601V from Cytonix, or 1.7% Cytop CTL-809M from Asahi Glass) was spin-coated and baked to form a ~50 nm-thick hydrophobic layer on top. The baking was done at 330°C for 1 hour for the Teflon, at 120°C for 30 min for the FluoroPel, and at 150°C for 20 min and then at 195°C for 1 hour for the Cytop, all following the manufacturers' recommendations.

2.2. Experimental Setup

The overall experimental setup is described in figure 1. The contact angle of the droplet was captured with a back illumination by a DDC camera (PixeLink, model PL B742U) for analysis. The EWOD actuation signals were generated by a DAQ (National Instruments) controlled by a LabVIEW program and then amplified by an amplifier (TREK, PZD700) to the desired voltage level. Three voltage types were used, as shown in figure. 2(a) – (c): +30 V_{DC}, -30 V_{DC}, and 30 V_{AC} (peak-to-peak) of 1 kHz square wave. The applied voltage of 30V corresponds to an electrowetting number *Ew* of 0.336, 0.338, and 0.340 on the EWOD samples coated with Teflon, FluoroPel and Cytop, respectively, and is lower than the observed saturation voltage of 40-50 V, corresponding to *Ew* of ~ 0.5. By using square wave for AC voltage, the maximum force at the triple contact line (TCL) is the same as DC. For all the voltage types, a pulse actuation of 6 sec period with 50% duty cycle was repeated for 2000 cycles, i.e., 200 min. The conductive wafer was bonded on a copper tape and electrically grounded; a positive sign indicates that a higher potential is applied to the droplet. A 10 μL droplet mixture of glycerine and 0.1M KCl standard solution (1:1 volume ratio) was used to minimize the evaporation. During the 2000 cycles of actuations, there was no noticeable volume change of the droplet. Also, this mixture has electrical conductivity of 0.013 S/m, conductive enough to ensure that voltage drop across the droplet is negligible. Each of all the data points reported in this work is an average over four repeated experiments using four different devices, i.e., each experiment using a new device.

3. Result

3.1. Performance on different hydrophobic layers

3.1.1. Positive DC

Contact-angle data on the three hydrophobic layers with positive DC are plotted in figure 3(a). In general, the contact angles with the voltage removed (i.e., V_{off}; EWOD is off) decreased rapidly in the initial ~150 cycles and then very slowly for the rest. However, the contact angles with the voltage applied (i.e., V_{on}; EWOD is on) increased throughout the 2000 cycles. After quickly increasing during the first ~70 cycles, the increase on Cytop was at a much slower rate, compared with Teflon and FluoroPel. Because the electrowetting effect is the difference between the contact angles at V_{off} and V_{on}, the degradation can be compared more clearly using contact-angle reduction, as plotted in figure 3(d). During the initial 500 cycles, Teflon and FluoroPel showed slightly larger contact-angle reductions than Cytop. After 500 cycles, however, Cytop provided larger contact-angle reductions than the other two, showing considerably slowed down degradation after ~200 cycles.

3.1.2. Negative DC

Contact-angle data on the three hydrophobic layers with negative DC are plotted in figure 3(b). In general, the contact angles at V_{off} decreased in the initial ~250 cycles and then decreased very slowly for the rest, similar to the positive DC case. However, the contact angles at V_{on} did not significantly increase for the first few hundred cycles, unlike the positive DC case. On Teflon and FluoroPel, the contact angles at V_{on} started to increase after ~500 and ~800 cycles, respectively, and reached close to the contact angles at V_{off} by 2000 cycles. On Cytop, in comparison, the contact angles at V_{on} increased much less – only 2° over the entire 2000 cycles. The contact-angle reductions in figure 3(e) show the degradation is much less on Cytop.

3.1.3. AC 1 kHz

Contact-angle data on the three hydrophobic layers with the 1 kHz AC are plotted in figure 3(c). In general, the contact angles at V_{off} decreased in the initial ~200 cycles and then decreased very slowly for the rest, similar to the DC cases. The contact angles at V_{on} increased mildly in the first ~1000 cycles and then remained unchanged for the rest of the cycles. Unlike the DC cases, all three materials showed the same trend of contact-angle reduction, as shown in figure 3(f): 14°-16° at the 1st cycle, 12°-13° after ~100 cycles, and 9°-10° after 2000 cycles. The data suggest that the degradation is the same for all the three materials under the given AC voltage and pattern.

3.2. Performance under different voltage types

The data of contact-angle reduction are re-plotted in figure 4 to compare the effect of voltage types applied. For Teflon (figure 4(a)) the negative DC provided the best performance for the first ~700 cycles, after which the degradation accelerated for the rest of the cycles. After 1000 cycles, the AC remained the most effective. For FluoroPel (figure 4(b)) the negative DC provided the best performance for the first ~1000 cycles and the degradation accelerated after ~800 cycles, similarly to the case of Teflon. The AC remained the best as well after 1000 cycles. For Cytop (figure 4(c)) the positive and negative DC had the worst and the best performance, respectively. Although negative DC provided larger contact-angle reductions throughout most of the cycles, its degradation seemed worsened to approach the AC case after ~1800 cycles. However, contact angles after the 2000 cycles have not been investigated. It is interesting that the contact-angle reduction for the 1 kHz AC was between those of negative and positive DC for the first ~1000 cycles on Teflon or FluoroPel and throughout the 2000 cycles on Cytop.

4. Discussion

4.1. Contact angles without and with applied voltage

As the EWOD voltage was applied repeatedly in our tests, the contact angles at V_{off} decreased fast during early cycles and then decreased very slowly for the rest of the experiment regardless of hydrophobic material and voltage type. However, the contact angles at V_{on} depended on the hydrophobic layer and voltage type. On Cytop, the contact angles at V_{on} increased somewhat fast in early cycles and then slowly over time (figure 3(a), (b) and (c)). This trend agrees well with the tests on Cytop (although in oil ambient) by Berry et al. [15], where they applied a voltage larger than the theoretical threshold determined by the dielectric strengths and thicknesses of the main dielectric and the hydrophobic layer. According to Verheijen and Prins [12], trapped charges in the insulating layer shield the electric field, weakening the electrowetting force. They showed the slope of potential changes by the trapped charges and the decrease of electric field near the solid-liquid interface. Based on their theory, at V_{off} the embedded charges would create an electrowetting effect and reduce the off contact angle, $\theta_{V_{off}}(N)$, slightly. At V_{on} they would shield the electric field created by the external voltage and compromise the contact-angle reduction, i.e., increase the on contact angle, $\theta_{V_{on}}(N)$.

4.2. Hydrophobic material

The degradation, i.e., a gradual decrease of the contact-angle reduction, was found dependent on hydrophobic materials under our test conditions. Since the dielectric constants of all three tested materials are similar (1.93-2.1), the contact-angle reductions in the first cycle (i.e., before any charge is imbedded) were almost the same regardless of the material. However, after repeated actuations, Cytop performed better than the other two under the DC actuations. This also agrees with that of Berry et al. [13] despite different test conditions. Seyrat and Hayes [16] also reported that Teflon AF 1600 loses its EWOD performance quickly for a layer thinner than 400 nm. Electrical properties of Teflon, FluoroPel and Cytop, as well as the electric field applied across each of them during the tests in this work, are listed in table 1. We calculated the electric field applied across the fluoropolymer layers considered voltage division in the dielectric layer and the dielectric strength of each material. The electric field in the Teflon layer (0.092 V/nm) was much higher than its dielectric strength (0.021 V/nm) while those across the FluoroPel (0.089 V/nm) and the Cytop (0.085 V/nm) were below their dielectric strengths (0.17 V/nm and 0.11 V/nm, respective). There is no clear explanation why Teflon did not perform worse than FluoroPel, other than noting that the dielectric strengths used in the calculation are from other sources. In addition to the issue of dielectric strength and perhaps more importantly, we note that Cytop has the lowest resistivity among the three. We hypothesize that electrically leakier Cytop diffuses the trapped charges better than the other two, exhibiting the best performance.

4.3. Voltage type

The performance of EWOD depended on the applied voltage type as well. Comparing the polarity of DC voltage, the contact-angle reduction degraded always less with negative DC than positive DC. The polarity dependence of EWOD actuation has been reported by many groups. According to Moon et al. [14], the electrowetting curve deviated from the theoretical curve more in a positive DC, and they assumed it was due to the adsorption of hydroxide ions, OH-, on the Teflon AF surface [17]. Quinn et al. [18] also reported asymmetric electrowetting curves in positive DC and implied this deviation was observed only in positive DC due to adsorbed negative ions. Moreover, S. Chevalliot et al. [19] compared the electrowetting curves of DC and AC in oil ambient showing they deviate at high voltage and reach different contact-angle saturation. In addition, the performance degradation with 1 kHz AC actuation was in between those of positive and negative DC cases in early cycles. However, in the end the AC actuation performed better for all three hydrophobic materials. We speculate that the characteristic of AC voltage, regularly changing polarity, helps discharging the trapped charges. One interesting point is that despite the superior performance of Cytop under negative DC all the three tested hydrophobic materials performed similarly under AC voltage – an observation not yet satisfactorily explained.

5. Conclusion

In general, the contact angle at V_{off} ($\theta_{V_{off}}(N)$) decreased and the contact angle at V_{on} ($\theta_{V_{on}}(N)$) increased over repeated actuations, and these phenomena can be explained using the charge trapping model suggested by Verheijen and Prins [12]. While $\theta_{V_{off}}(N)$ degraded very slowly for all cases, $\theta_{V_{on}}(N)$ highly depended on hydrophobic top coating and voltage type. In comparison to FluoroPel and Teflon, Cytop showed superior long-term EWOD performance under the tested conditions. The low resistivity of Cytop suggested that the electrically leakier topcoat would help the long-term EWOD performance. The results also indicated that electrowetting in 1 kHz AC is preferred over DC for long-term actuations due to slow degradation

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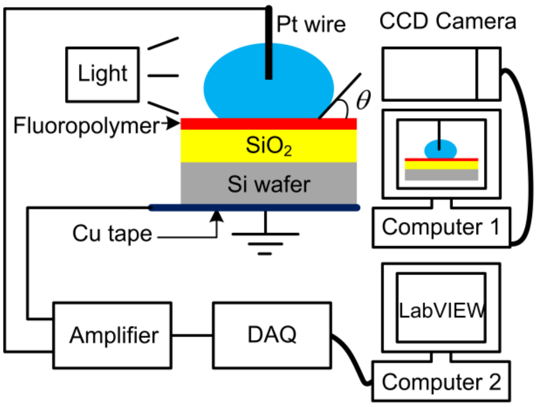


Figure 1. Experimental setup for the repeated EWOD actuation with programmed monitoring of the contact angle.

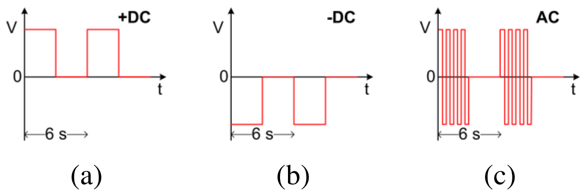


Figure 2. Three types of voltage signals: (a) positive DC, (b) negative DC, (c) 1 kHz AC.

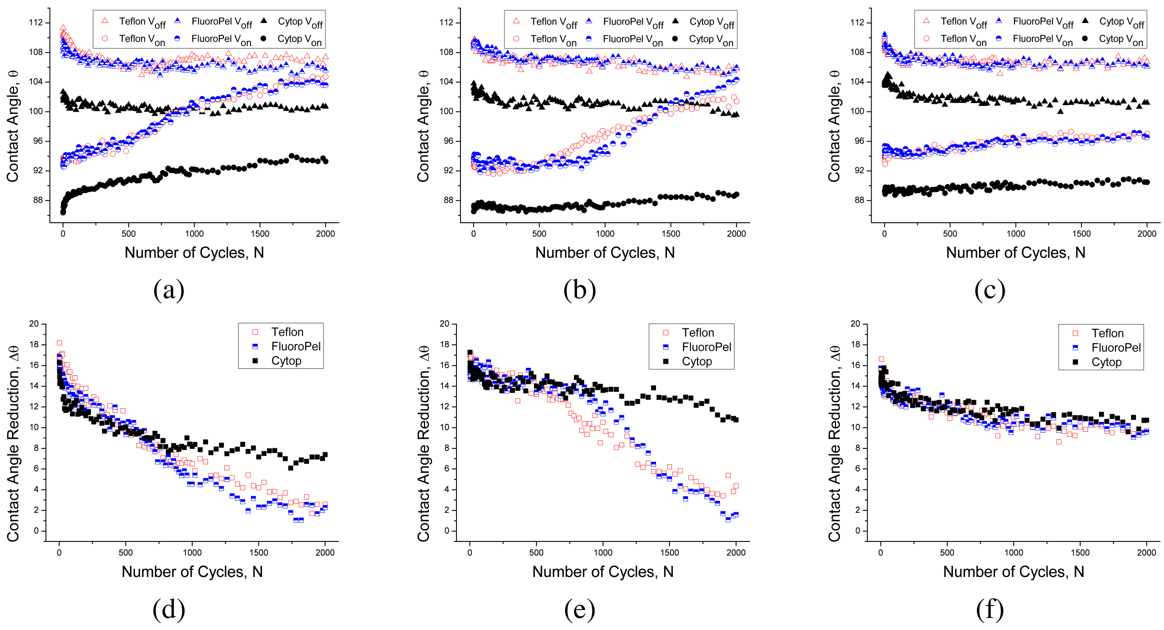
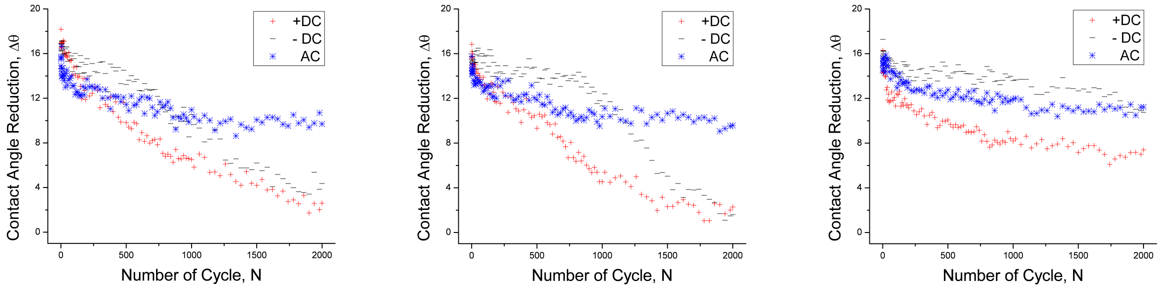


Figure 3. EWOD responses: (a) Contact-angle data with +DC; (b) Contact-angle data with –DC, (c) Contact-angle data with 1 kHz AC, (d) Contact-angle reduction with +DC, (e) Contact-angle reduction with –DC, (f) Contact-angle reduction with 1 kHz AC. Note the contact-angle reduction $\Delta\theta$ degrades over the actuation cycles N in (d-f).



(a) (b) (c)

Figure 4. Degradation of contact-angle reductions by three types of actuation on (a) Teflon, (b) FluoroPel and (c) Cytop.

Table 1. Electrical properties of Teflon AF 1600, FluoroPel 1601V and Cytop CTL-809M. [20-23]

	Teflon	FluoroPel	Cytop
Dielectric constant	1.93	2.0	2.1
Dielectric strength (V/nm)	0.021	0.17	0.11
Electric field applied* (V/nm)	0.092	0.089	0.085
Volume resistivity (Ω cm)	$>10^{18}$	$>10^{18}$	$>10^{17}$

* Voltage across the fluoropolymer top coating (calculated) divided by its thickness (50 nm). The main dielectric layer underneath the fluoropolymer is 560 nm-thick silicon dioxide.