Reliable and low-voltage electrowetting on thin parylene films

Manjeet Dhindsa a,b,1, Stein Kuiper b,2, Jason Heikenfeld a,⁎

a University of Cincinnati, Novel Devices Laboratory, School of Electronics and Computing Systems, Cincinnati, OH 45221, USA
b Philips Research Eindhoven, High Tech Campus 34, 5656 AE Eindhoven, The Netherlands

Abstract

The stability of an electrowetting system is dependent upon the choice of liquids, the dielectric material and the operating voltage. Substantial progress is reported herein on use of 300 nm thick poly(α, α, α′, α′-tetrafluoro-para-xylylene) (Parylene HT) films for almost 100° of reliable electrowetting modulation at only 15 V. Not only does Parylene HT exhibit improved resistance to dielectric failure as compared to poly(2-chloro-para-xylylene) (Parylene C), but Parylene HT is shown to sustain continuous DC electrowetting to ~70° for >6 h. Furthermore, Parylene HT has a surface energy such that when electrowetting in an alkane oil ambient, a Young's angle of about 170° can be achieved without the traditional fluoropolymer topcoat. Also presented is a discussion of electric field enhancement when electrowetting in an oil bath. It is shown that Parylene HT is a promising candidate for low-voltage and large-area electrowetting devices such as displays and lab-on-chip.

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1. Introduction and background

Parylene is a vapor deposited and conformal dielectric that is well known for its use as a hermetic seal. Good electrical insulation and resistance to water permeation has made parylene one of the most extensively used dielectrics in electrowetting systems [1–3]. Furthermore, parylene has also been shown as commercially viable in Varioptic’s variable-focus electrowetting lenses [4]. Many previous reports and Varioptic’s lens target applications where parylene can be thick (several μm) because use of 30–60 V for operation is not an issue. In an electrowetting system Young’s angle (\(\cos \theta_Y = (\gamma_{oa} - \gamma_{ad})/\gamma_{ao}\)) is reduced to the electrowetted contact angle (\(\theta_V\)) as predicted by the electrowetting equation [5,6] \(\cos \theta_Y = (\gamma_{oa} - \gamma_{ad})/\gamma_{ao} + \epsilon V^2/(2d\gamma_{ao})\), where: \(\epsilon\) is the dielectric constant and \(d\) is the thickness of the dielectric respectively; \(\gamma\) is the interfacial tension between the electrowetting liquid (a, typically aqueous), the oil surrounding the electrowetted liquid (o), and the dielectric (d); \(V\) is the applied DC or AC RMS voltage. The electrowetting equation predicts that thicker dielectrics and higher voltages do not increase the energy required for achieving a given \(\theta_V\). From that point of view, for applications such as a lens in a camera phone, using a step-up voltage converter is not of major concern. However, such converters themselves consume quite some energy.

⁎ Corresponding author. Tel.: +1 513 556 4762, +1 513 556 4990; fax: +1 513 556 7326.
E-mail address: heikenjc@ucmail.uc.edu (J. Heikenfeld).
1 Tel.: +1 513 556 4990; fax: +1 513 556 7326.
2 Tel.: +31 40 274 7886.

Fig. 1. Dielectric materials and testing set-up: (a) molecular structure of Parylene C vs. Parylene HT monomers; (b) dielectric failure testing; (c) electrowetting contact angle testing.
Recently, a growing number of electrowetting applications require very large arrays of thousands or millions of electrodes [7]. Examples include electrowetting displays [8], electroluidic displays [9] and a programmable lab-on-chip platform [10]. In large arrays, typically active-matrix electrode control is required. Active-matrix addressing uses a matrix of columns and scanning row electrodes with intersections at the gate and source of thin-film-transistors [11]. As demonstrated for liquid crystal displays (LCD), the transistor drain can provide 8-bit voltage control at each location in the array. Thin-film transistors, however, conventionally provide reliable operation up to about only 15 V. Therefore, the parylene dielectrics that work well at thicknesses of several microns must be reduced in thickness if 15 V operation is to be achieved. Thickness reduction of dielectrics in electrowetting systems can be unconventionally challenging. As predicted by the electrowetting equation, reducing the dielectric thickness increases the electric field across the dielectric to achieve a given $\theta_e$, thus increasing the probability of charging effects and dielectric breakdown. Furthermore, as the dielectric thickness decreases, eventually the thickness of the dielectric can be similar to the size of voids or pin-holes in the dielectric, thus causing dielectric failure when voltage is applied. Ultra-thin film dielectrics are, therefore, generally not reliable in electrowetting systems. The electrowetting equation suggests that using high-$\epsilon$ dielectrics could also reduce the voltage. However, in combination with a hydrophobic top coat this option turns out to have no effect [12], because of field amplification in the top coat.

The Cincinnati group has previously shown that on a stack of atomic-layer-deposited $\text{Al}_2\text{O}_3$/Asahi CYTOP 809 M fluoropolymer, reliable low voltage (~15 V) electrowetting can be achieved by using ion and liquid molecules that are large [13], and which therefore have difficulty migrating through the dielectric stack. However, two issues remain. First, atomic-layer-deposition is a low-temperature and reliable process, but it is typically not economical beyond use in semiconductor devices. Secondly, in many applications, such as Lab-on-Chip, it is desirable to use small-molecule electrowetting liquids such as water, containing small ions such as KCl which can cause premature failure of the dielectric [13]. Therefore improved dielectric options are needed.

Presented herein are thin parylene films that can reliably provide 100° of contact angle change at ~15 V operation. In particular, poly($\alpha$, $\alpha'$, $\alpha''$-tetrafluoro-para-xylene) films (obtained from Specialty Coatings Systems, Inc., tradename Parylene HT) show superior resistance to dielectric failure. Also demonstrated, Parylene HT reduces undesirable contact angle relaxation [14], even over a period of 6 h of continuous application of DC voltage well above the saturation voltage. Parylene HT is also stable in air up to 350 °C (up to 450 °C for short term), therefore allowing 180 °C annealing of thin fluoropolymer top coats such as Asahi CYTOP and DuPont Teflon AF. Furthermore, by interfacial tension matching [15] Parylene HT with an alkane oil, almost 100° of electrowetting modulation is achieved without a fluoropolymer top coat. As part of the analysis, also presented herein is a simple model for electric field enhancement at the contact line when electrowetting in an oil bath. At present, the demonstrated attributes for Parylene HT appear to be superior to plasma-deposited fluorocarbon dielectrics [16]. Parylene HT could be an ideal solution for numerous low-voltage electrowetting applications requiring a scalable and economical dielectric deposition process.

2. Materials and experimental method

Electrowetting substrate samples were prepared using the following procedure. Substrates were aluminosilicate glass coated with a transparent conducting electrode SnO$_2$:In$_2$O$_3$ (100 Ω/square, 150 nm thickness) purchased from PGB&Co Inc. The substrate/electrode was next coated with parylene film by dimer vaporization and vapor pyrolysis, followed by room-temperature monomer deposition and polymerization on a surface at 13.3 Pa. Inherent to the deposition process is particulate formation due to spontaneous polymerization in the gas phase. These particulates tend to precipitate. For that reason, samples to be coated are placed in the parylene coater facing downward. Tested films included the commonly used poly (2-chloro-para-xylene) (Specialty Coatings Systems, Inc., trade name Parylene C) having a monochlorinated aromatic ring ($\gamma_o = 38$ mN/m), and the less commonly used Parylene HT in which fluorine atoms replace all aliphatic hydrogen atoms ($\gamma_o = 22$, $\gamma_o = 26$ mN/m) (data, Specialty Coatings Systems, Inc.), both shown in Fig. 1a. The other variants Parylene N and Parylene D differ from Parylene C by only one chlorine atom and are not shown or tested herein. Both 700 nm and 300 nm thickness were tested, resulting in a total of four sample sets. Some of the Parylene HT samples for contact angle measurements were further coated with a ~50 nm fluoropolymer layer, by dip-coating with Cytonix FluoroPel 1601 V solution, followed by a 120 °C bake for 20 minutes ($\gamma_o = 14$ mN/m). As illustrated in Fig. 1b and c, a DC voltage was applied to the aqueous droplet in air (1 μl, ~5 mm$^2$ base area while electrowetted) using a Pt wire. The SnO$_2$:In$_2$O$_3$ electrode was electrically grounded. For dielectric failure testing, an HP 4140 B picoammeter was connected as shown in Fig. 1b, and voltage was ramped at a step rate of ±2 V/2 s, from 0 to ±80 V. At the high voltages used for dielectric failure testing, inhomogeneous charge injection or dielectric failure can cause the droplet to horizontally leap away from the Pt probe tip. In an oil bath, droplet leaping occurs easily due to the low contact angle hysteresis and smaller adhesion forces to the probe tip. For these reasons dielectric failure tests were performed in air. For electrowetting contact angle testing, lower voltages are used and therefore measurements could be performed in a bath of alkane oil (1:1 blend of Fisher Scientific dodecane and tetradecane, $\gamma_o \approx 25$ mN/m) or a silicone oil (8:1:1 blend of Dow Corning OS 20/OS 10/OS 30, $\gamma_o \approx 16$ mN/m). The voltage ramp for electrowetting was ±1 V/2 s and contact angles were captured and calculated using a VCA Optima measurement system (Fig. 1c). All measurements were done with a solution of sodium dodecyl sulphate (SDS) in water (0.013 wt.%) and 1.00 wt.%). This surfactant is commonly used to reduce the required voltage compared to pure water and is therefore chosen for the investigation of its affect on dielectric failure.

3. Theoretical considerations for electric field

Unlike typical capacitive devices, there are two unique attributes to electrowetting systems that cause increased electric field as the dielectric thickness is reduced. Firstly, as dielectric thickness ($d$) is reduced, the electric field required for achieving a given $\theta_e$ increases proportionally to $1/d^{1/2}$. As plotted in Fig. 2, the electric field underneath the droplet should double to a value of ~50 V/μm as the parylene thickness $d$ is reduced from 0.8 to 0.2 μm (1.00 wt.% sodium dodecyl sulphate (SDS) surfactant, alkane oil system, $\theta_e = 180^\circ$, $\theta_e = 70^\circ$, $\gamma_o = 6$ mN/m [17]).

Secondly, for thin dielectric films such as those under consideration, dielectric failure calculations must also consider the enhanced electric field [18] similar to the edges of planar metal electrodes and at the tips of field emission devices [19]. During electrowetting, on a microscopic scale $\theta_e$ is unaltered [20], and the meniscus transitions from $\theta_e$ to the macroscopically observed $\theta_e$ over a distance comparable to dielectric thickness $d$. If we assume that in this transition area the meniscus has a constant radius of curvature $R$ and the microscopic contact angle $\theta_e = 180^\circ$, the situation as provided in Fig. 3 is obtained. With simple trigonometry $R$ can be related to dielectric thickness $d$ according to $R = d/(1 + \cos\theta_e)$. Hence, the thinner the dielectric $d$, the smaller the radius of curvature $R$, and the greater the enhanced local electric field. This could imply that at the edge of the droplet the electric field increases stronger than $1/d^{1/2}$ for decreasing $d$. A fully quantitative analysis of this field enhancement is beyond the scope of
thickness. The breakdown electric voltage and vs. dielectric thickness; (b) electric field beneath the droplet vs. dielectric thickness. The breakdown electric field (Ebr) of parylene is also shown.

this publication. However, this observation will be of value for discussion of the experimental results.

4. Experimental results — dielectric failure

For the initial set of experiments, an aqueous solution of 0.013 wt.% SDS was tested. As previously reported, this concentration of SDS is sufficient for resolving the difference in currents between positive and negative DC voltages while investigating the ion size dependency of dielectric failure [13]. Shown in Fig. 4a, 700 nm of Parylene C and HT each exhibited no dielectric failure (1 < 0.01 μA/mm²) up to ±80 V. Therefore, the thinner 300 nm Parylene C and HT were tested. As shown in Fig. 4c, for 300 nm of Parylene C, a positive voltage (i.e. the droplet has a higher potential than the electrode) below 10 V shows an increase in the current across the dielectric. This indicates the onset of small hydrated Na⁺ ions being driven through the dielectric, similar to that previously observed for Al₂O₃ dielectrics [13]. At negative voltage, charge injection into the dielectric is much smaller due to the large size of the dodecyl sulphate ions [13]. The low voltage (< 10 V) required for the onset of current increase is surprising, because the 700 nm layer does not show any current increase, even at 80 V. This indicates that defects in the layer play a major role in the breakdown mechanism.

Next, 300 nm Parylene HT samples were tested with 0.013 wt.% SDS solution and no dielectric failure was observed for positive or negative voltages (Fig. 4d). For that reason, the SDS concentration was increased to 1.00 wt.%, which is much higher in ionic content and is more commonly used to lower the electrowetting voltage through decrease in interfacial tension. Dielectric failure was not observed until about +50 V. Compared to Parylene C, not only does Parylene HT require a higher conductivity solution (more SDS) to observe dielectric failure [13], but the dielectric failure is much more predictable. Additionally, 1.00 wt.% SDS leads to a lower contact angle than 0.013 wt.% SDS which may also be a cause for the failure (field enhancement at the contact line). A similar field enhancement for smaller contact angles may explain why Parylene C fails at lower voltages than Parylene HT. However, the breakdown experiments revealed no statistical preference for the location of the electrical breakdown (underneath the droplet vs. near the contact line, as observed by electrolysis and bubble formation). This is surprising, because dielectric failure tests were performed in air with a θp of only 43°–55°, which therefore causes a sharp liquid wedge geometry with zero radius of curvature at the wedge tip (R = 0). Therefore, for the experimental conditions explored herein, edge enhanced electric field does not seem to play a significant role in dielectric failure. This suggests that dielectric failure in thin Parylene films is site (defect) dependent and not purely a bulk material effect.

Parylene HT is known to penetrate holes much deeper than Parylene C, due to a lower sticking probability. Hence during deposition it may have a tendency to fill its own voids resulting in a higher film quality in comparison to Parylene C. It is clear that Parylene HT is superior to Parylene C when tested with an aqueous SDS solution. This hypothesis is supported by the fact that the percentage of water absorption for Parylene HT is less than 0.01% after 24 h, whereas the percentage of water absorption for Parylene C is less than 0.1% (Internal company data, courtesy Specialty Coating Systems, Inc.). To conclude, the test results for Parylene HT were deemed promising because failure at 50 V is more than 3 times higher than the targeted electrowetting voltage (< 15 V). A further understanding of dielectric failure is not required at this point, because from a practical standpoint, the performance observed for Parylene HT is quite good. With good resistance to dielectric breakdown, electrowetting performance for thin Parylene HT dielectrics was next explored.

5. Experimental results — electrowetting

In the initial set of electrowetting experiments, Parylene HT was tested without a fluoropolymer top-coat. As reported by Maillard et al [15] the dominant requirement for achieving a large Young’s angle θy and with that a low contact angle hysteresis, is to use an oil that exhibits...
a low interfacial tension with the dielectric. To achieve such a low interfacial tension \( \gamma_{od} \) with the Parylene HT surface \( \gamma_d = 26 \text{ mN/m} \), we utilized a 1:1 mix of n-dodecane and n-tetradecane (both Fisher Scientific) \( \gamma_o \approx 25 \text{ mN/m} \) As shown in Fig. 5a with a 0.013 wt.% SDS aqueous solution \( \gamma_{ao} = 17.6 \text{ mN/m} \), measured via pendant droplet method, excellent electrowetting can be achieved down to \( \theta_v = 90^\circ \) at ±30 V. It must be noted here that the electrowetting response was found to be fairly linear in contrast to the theoretical prediction of the electrowetting equation. Lower angles may be possible, but the droplet would horizontally leap from the Pt wire electrode (presumably due to inhomogeneous charge injection). A 1.00 wt.% SDS solution was also tested \( \gamma_{ao} = 6 \text{ mN/m} \) and only about 15 V is required to reach \( \theta_v = 80^\circ \) (Fig. 5b). This result now satisfies the voltage requirements stated in the introduction section of this article. However, the droplet still leaped away from the Pt probe at 19 V.

For most electrowetting applications the electrowetting device geometry uses liquids in a manner where droplet leaping is not an issue. Regardless, we next pursued a means to prevent droplet leaping. Fig. 5c is a plot of electrowetting results with addition of ~50 nm thick FluoroPel 1601 V top-coat \( \gamma_d = 14 \text{ mN/m} \) on the Parylene HT film, and using a silicone oil blend \( \gamma_o \approx 16 \text{ mN/m} \) that is more closely matched to the FluoroPel surface than the alkane blend. A stable and symmetric contact angle reduction to \( \theta_v \approx 90^\circ \) was achieved with ±15 V for a 1.00 wt.% SDS solution. The electrowetting could be driven well into contact angle saturation at \( \theta_v = 60^\circ \) without droplet fly-off. After ramping up the voltage to ±30 V, the voltage was
6. Experimental results — continuous DC electrowetting

Generally, electrowetting practitioners avoid long term application of DC voltages because: (1) charge injection increases with time; (2) dielectric failure in electrowetting systems is typically propagating; (3) electric fatigue may occur, which is, for instance, observed in insulated metal cables. Longer duration electrowetting tests were performed for a drop of 1.00 wt.% SDS solution on 300 nm Parylene HT/50 nm Fluoropel stack, and the silicone oil blend. Three voltage schemes were investigated: +25 V DC, −25 V DC, and ±25 V AC (square wave, 1 kHz). These voltages were chosen because they are beyond electrowetting saturation at 20 V. As a result, the dielectric film will be stressed much further than during operation (0–15 V). Fig. 6 shows a time lapse images of the droplet for each voltage scheme over a time period of 50 s to 6.5 h. An initial θY of −165° is obtained for each scheme as expected. For positive DC voltage (Fig. 6a), the droplet continues to stay wetted at 70° without any contact angle relaxation even after 50 s. However there is a loss of 15° when the voltage is switched to 0 V, which indicates charge injection into the dielectric stack equivalent to −4 V. Due to this significant charging, this positive DC test was not continued any further.

For negative DC voltage (Fig. 6b), the droplet wets to 68° and maintains this contact angle for 50 s, while reaching the initial θY when the external voltage is set to 0 V. These results indicate that a negative DC voltage exhibits substantially less charge injection. After about 10 min of continuous negative DC voltage, the electrowetting contact angle remains 68°, but θY is reduced by 15° when the external voltage is set to 0 V. This result shows that also for negative voltages charge injection occurs, although it takes much longer than for positive voltages. After 6.5 h the droplet still exhibited almost no relaxation of the electrowetted contact angle. There is however −25° loss in final contact angle when the voltage is switched to 0 V. Even though this is equivalent to 5.5 V of injected charge, being able to modulate between 140° and 70° using only DC voltage may be attractive for numerous electrowetting applications.

For 1 kHz AC voltage (Fig. 6c), the droplet wets to the lowest contact angle of 50°, evidence of less charge injection due to the alternating electric field, and maintains this angle for 50 s, while reaching the initial θY as the voltage is switched to 0 V. There is an interesting observation of minor electrolysis at the probe that self heals (bubble formation stops) within 20–25 s. This behavior remains quite reproducible and is still not understood. After 10 min no relaxation in the electrowetting contact angle is observed. After 2 h, the droplet did, however, undergo massive electrolysis and physical surface deterioration as seen in the image. Electrical fatigue could be one of the mechanisms for this breakdown effect. Another cause may be the lower contact angle, resulting in field enhancement at the droplet edge. It is evident from this data that Parylene HT with negative DC voltage shows excellent reliability. As reported previously [13], the positive and negative DC performance might be even further improved by moving to non-aqueous solutions with both large molecule cation and anion (SDS has a small cation, Na+).

7. Summary

This study demonstrates that Parylene HT is a robust electrowetting dielectric in terms of dielectric failure and charge injection. With 300 nm of Parylene HT electrowetting devices can operate at low voltage (15 V), thereby allowing the use of active-matrix addressing with thin-film transistors. It was also shown that with proper choice of oil, Parylene HT can achieve 100° of electrowetting performance even without a traditional top-coat of fluoropolymer. The results reported herein are particularly compelling for use in displays [8,9] and programmable lab-on-chip [10], because these applications require a reliable, scalable, and low-cost dielectric.

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Fig. 6. Electrowetting lifetime tests. 1 μL droplet of 1.00 wt.% SDS solution in silicone oil is tested for 50 s to 6.5 h on 300 nm of Parylene HT coated with ~50 nm of Fluoropel. Three voltage schemes (a) +25 V DC, (b) −25 V DC and (c) 25 V AC are shown. Negative DC voltage shows the most reliable response with almost no relaxation (Δθ = 100°) for 6.5 h and AC exhibits the lowest contact angle (51°) but dielectric failure after 2 h.

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