Octadecylphosphonic Acid Self-Assembled Monolayers in Low Voltage Electrowetting-on-Dielectric Systems

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Octadecylphosphonic acid reacts with oxidized aluminum surfaces to form a self-assembled monolayer film. The effectiveness of the monolayers are examined for use in an electrowetting-on-dielectric application using anodized aluminum as the substrate. We report growth of the monolayers by monitoring contact angle and SEM imaging. Electrowetting is characterized in static and dynamic configuration, giving advancing, receding, and contact hysteresis. The films greatly reduce the voltage requirement for drop movement, but the high hysteresis currently limits the effectiveness at low voltage operation.

Introduction

Electrowetting-on-Dielectric (EWOD) refers to the change in apparent contact angle when a voltage is applied between a conductive liquid drop and a dielectric coated electrode. An EWOD system is comprised of a conductive base electrode, a dielectric layer, and the electrolyte that is electrically connected through an external circuit to the base electrode. The dielectric layer must be hydrophobic in order to provide for a large contact angle change and drop movement. Commonly fluoropolymers (e.g., Teflon) are used for the hydrophobic layer; these coatings exhibit initial contact angles in excess of 100°, allowing easy drop movement. The EWOD effect is described by the Lippmann-Young expression quantifying the contact angle dependence on applied voltage:

$$\cos(\theta) = \cos(\theta_0) + \frac{C V^2}{2 \gamma_{lg}} = \cos(\theta_0) + \frac{1}{2 \gamma_{lg}} \frac{\varepsilon_r \varepsilon_0 V^2}{t}$$

[1]

where $\theta$ is the apparent contact angle of the liquid under applied voltage, $\theta_0$ is the equilibrium contact angle, $\gamma_{lg}$ is the surface tension at the gas-liquid interface, $\varepsilon_r$ is the dielectric constant of the dielectric layer, $\varepsilon_0$ is the permittivity of free space, $t$ the thickness of the dielectric layer, and $V$ is the applied voltage. As evident from Equation 1, EWOD performance greatly depends on the capacitance of the dielectric layer and the initial contact angle. A main concern in high performance operation is the breakdown field strength of the dielectric layer, which should limit, according to Eq. 1, the maximum value of the contact angle change. In addition, dielectric failure when the field strength is exceeded would destroy any future reversible operation. Therefore, most electrowetting applications employ dielectric layers of thicknesses exceeding one micron, which may sustain applied voltages in excess of 200V and achieve large contact angle change (1).

A method to reduce the voltage requirement utilizes significantly thinner materials while increasing the dielectric constant. Aluminum oxide has a breakdown field greater...
than 6MV/cm with a dielectric constant of 9; with such properties this material would ideally achieve 30° of contact angle change with only 5V. The EWOD system however would require a hydrophobic layer to set up a high initial angle, adding a series capacitance with the oxide. When the two layers are in series, the hydrophobic layer becomes the limiting component, since the dielectric constant of most fluoropolymers is ~2. The use of Self-Assembled Monolayers (SAM) may reduce the thickness of the dielectric to approximately 2nm, dependent on the actual molecule orientation, greatly enhancing the EWOD response at low voltage. Organophosphonic acids have shown to strongly interact with oxidized Al surfaces in both polar and nonpolar solvents, bonding via a condensation reaction between the phosphoric acids and the oxide surface hydroxyl groups (2). This work investigates the behavior of octadecylphosphonic acid (ODPA) as the hydrophobic layer for an anodic aluminum oxide based EWOD system.

**Experimental**

Aluminum films (100 nm) were grown by e-beam evaporation (CHA Industries, Fremont, CA) onto the native surface of a Si wafer, pre-coated with a 5nm thick titanium adhesion layer. Aluminum anodization was performed in 30 wt% ammonium pentaborate (NH₄B₅O₈) in 99.8% ethylene glycol at room temperature using a vertically oriented two electrode electrochemical cell using a platinum mesh counter electrode. The thickness of the resulting barrier film depends upon V and is calculated by the anodizing ratio (nm/V) and confirmed with a spectroscopic ellipsometer (HORIBA Jobin Yvon, Irvine, CA).

Octadecylphosphonic acid (97%) was purchased from Sigma-Aldrich, which was mixed as-received in Toluene (99.5%) at a 1mM concentration. The solution was heated and stirred until clear when the aluminum oxide films were placed in the monolayer solution for times ranging from 2-72hrs at various temperatures.

The contact angle of the SAM/Al oxide films was measured by placing a 10µL drop of Milli-Q water on the clean surface. A Ramé-Hart Goniometer Model-200 (Succasunna, NJ) was used to image the drop and calculate the contact angle using their analysis software, DROPimage Standard. Static electrowetting measurements were performed by using the goniometer system in conjunction with a Kepco power source and a Keithley 2001 to monitor current using 10µL drops of a .05M sodium sulfate solution. Dynamic Measurements used the Wilhelmy Plate method in a Krüss tensiometer (Hamburg, Germany) at an immersion rate of 3mm/min. Imaging in a scanning electron microscope was performed at low-voltage (500V) with a field emission FEI Quanta 650 SEM (Hillsboro, Oregon).

**Results & Discussion**

**Dielectric Formation and Characterization**

The aluminum oxide layer was fabricated by electrochemical anodization of a precursor aluminum layer grown by e-beam evaporation. The applied voltage determines the final oxide thickness according to the anodization ratio of ~1.2nm/V, as confirmed by ellipsometry. In this study, a 44nm oxide layer was used as the base for the SAM fabrication; the electrical and electrochemical properties of the oxide layer has been established in a previous study (3). The 44nm thick film will allow for an operation voltage range greatly exceeding what is theoretically required for a 40° contact angle change. The
oxide film was confirmed as smooth and continuous, as determined by SEM imaging and X-ray reflectivity measurements.

Octadecylphosphonic acid (ODPA) layers were deposited on the aluminum oxide by submerging the films in a heated solution of toluene. Several different solutions were investigated for delivering the ODPA monomers, varying the solvent from non-polar to strongly polar, the solution temperature, and ODPA concentration. The film’s contact angles were evaluated over various immersion durations to determine the optimum fabrication conditions for use in EWOD measurements. Figure 1 shows the contact angle-time plot for samples formed in 1mM ODPA in Toluene at 45°C, showing contact angles reaching up to 110°. Each data point is the average of 6 measurements across the sample, and the error bar indicates the data range. Initially at low immersion time a large amount of scatter exists in the contact angle. As the immersion time increases the scatter in the data is drastically reduced, suggesting a SAM layer of high quality. The samples show the least scatter at highest angles between 28 and 42 hours; with longer immersion times however a decrease in contact angle occurs. The monolayer films likely progress from a disordered state at low immersion times to a continuous layer, to a multilayer configuration with a large amount of stacking at high immersion times, which reduces the contact angle.

![Figure 1. Average Contact Angle vs. immersion time of Al oxide samples in a 1mM ODPA–toluene solution at 45°C.](image)

The quality of the monolayer films was assessed using an SEM at low acceleration voltage (500V) for imaging. At low immersion times the films showed a generally flat surface without any discernable features with the exception of darker patches on the order of 100µm. These patches have been observed in a similar study (4), which described the region as multilayer stacking of the SAMs. Figure 2 shows images of two samples one at low immersion time (4hr) and the second after three days of immersion. The 4hr immersion sample (Figure 2a) shows what are likely three multiplayer regions; energy-dispersive X-ray spectroscopy (EDS) measurements on these regions detect strong Carbon and Phosphorus Kα signals, suggesting that these regions are indeed covered by a relatively thick layer of the SAM. For comparison, regions away from the dark spots show no P and very low C signal. Figure 2b shows the effect of an increase in immersion time; the monolayer stacking increases, showing large coverage of stacked layers.
Figure 2. SEM images of ODPA monolayer stacking on Al2O3 substrate (a) Onset of monolayer islands (b) after 3 days of immersion

Static Contact Angle Measurements

Electrowetting measurements commonly use a chemically inert needle inserted into the electrolyte drop as the top contact, while the metal substrate serves as the other electrode. In the static configuration the voltage is increased at a 1V step holding for 20s at each voltage. An image is captured using the goniometer at 10s after the voltage step is applied; the contact angle is subsequently analyzed through the Ramé-Hart ImageDrop software. The sample for this experiment was formed in 1mM ODPA-toluene solution at 45°C after 36hr immersion. Figure 3 summarizes the general electrowetting behavior observed for our monolayer-oxide system. The contact angle is shown on the right axis and the left axis displays the measured current. The electrowetting characteristics consists of three distinct regions, which we refer to as: low voltage, saturation, and desorption.

Upon initial increase of the voltage, the drop does not respond to the application of voltage; this is likely caused by the inhomogeneity of the monolayer film, inducing contact angle hysteresis. Upon the onset of motion, the response follows the theoretical Lippmann-Young curve (Eq. 1), which can be correctly predicted by fitting a series capacitance of the SAM and aluminum oxide layers. The contact angle change shown in Fig. 3 is still rather limited with an initial contact angle of 102° changing to only 89°.

Basic electrowetting theory predicts that the contact angle would change until the surface becomes completely wetted, but in actuality the contact angle reaches a limiting
angle, a phenomenon known as contact angle saturation (CAS). The CAS is typically defined by a deviation from the $V^2$ dependence observed in the low-voltage response. The origin of contact angle saturation is still debated, with theories invoking in turn a thermodynamic limit, drop ejection, or dielectric charging; a recent review shows invariance of saturation throughout test conditions (5), suggesting that no current model properly describes the observed phenomena. The saturation angles for most air-electrolyte systems ranges between 80-90 degrees with variation between measurements/samples. Once the system reaches saturation, the contact angle changes only slightly, until the eventual failure of the dielectric layer, as evidenced by the sharp increase in current above 30V.

The final region corresponds to a condition where the voltage exceeds the breakdown field of the aluminum oxide layer. This results in a current flowing through the aluminum oxide surface at high voltage, inducing gas evolution. Simultaneously, the monolayer desorbs from the oxide film, causing an irreversible decrease of the contact angle.

![Figure 3. Static electrowetting measurement of a .05M Na$_2$SO$_4$ drop on ODPA-44nm Al$_2$O$_3$ surface](image-url)
Dynamic Contact Angle Measurements

Dynamic contact angles describe three phase boundary motion giving “advancing” and “receding” contact angles, with their difference defining contact angle hysteresis (CAH). Commonly, in electrowetting CAH is studied by placing a droplet on a height gradient, monitoring the angles optically while the droplet slides, in a somewhat similar fashion to the static angle measurement. A less common measurement method due to sample design is the Wilhelmy method, where a sample is dipped into and out of a liquid bath. The tensiometer measures the total force as the plate is lowered into the liquid. The plate is formed by joining two monolayer-coated samples with a length significantly greater than the thickness of the films and substrate. The contract angle can be resolved from the measured force v. immersion depth of the sample through the following equations:

\[
F_{\text{Total}} = F_{\text{Wetting}} + F_{\text{weight}} - F_{\text{buoyancy}} \tag{2}
\]
\[
F_{\text{Wetting}} = \gamma_{\text{LG}} \cdot P \cdot \cos \theta \tag{3}
\]

where- \( \gamma_{\text{lg}} \) is the surface tension at the gas-liquid interface, and \( P \) is the wetted length.

The system removes the sample weight by weighing prior to insertion into the liquid. The effects of the buoyancy force are isolated by extrapolating the graph back to the zero depth of immersion. The remaining force is the wetting force allowing for contact angle determination. The advantage of using a system in this configuration allows for the entire contact line to contribute, which would give an average value of the contact angle across the entire sample. When measuring the contact angle directly, the angle is much more susceptible to variation by any minor changes on the surface.

The raw force-depth plot is shown in Figure 4 with the time of immersion varying from (a) 4 hours to (b) 24 hours. The force response in the 24hr immersion sample is similar to the response seen in hydrophobic polymer films, with a clear linear profile. The contact angle is calculated from the intercept of the force-depth curve using a linear extrapolation, giving an advancing angle of 112° and a receding angle of 88°. The 4hr sample shows a wide spread in contact angle, similar to the static contact angle in Figure 1. Averaging the curves gives an advancing angle of 104.2° and a receding angle of 80.4°. In both cases the contact angle hysteresis was nearly 25°, a very large value for application to EWOD systems. Fluoropolymers films commonly exhibit less than 10° hysteresis, allowing for minimal hindrance of drop motion. The large hysteresis in the SAM films is likely the cause for the lack of response in the low-voltage EWOD in Figure 3. For predictable EWOD performance, the hysteresis cannot alter the expected contact angle change.
Figure 4. Dynamic tensiometer measurement of ODPA – 44nm Al oxide (a) after 4 hr of immersion (b) after 24hr immersion in 1mM ODPA-Toluene solution.

Conclusions

ODPA monolayers were deposited on an anodic aluminum oxide reaching a contact angle of 109° in 45°C toluene solution. The electrowetting response required overcoming the greater than 20° contact angle hysteresis, causing no initial response at low voltage. After the onset of drop motion, the drop exhibited the expected Lippmann-Young response, until contact angle saturation and eventual SAM desorption. The hysteresis is likely caused by disorder in the monolayer films, especially at low immersion times where advancing and receding contact angles were observed to vary widely. For application in EWOD devices, the hysteresis must be greatly reduced by fabricating ordered films without stacking while reaching contact angles greater than 110°.

Acknowledgments

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References