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Journal
Journal of Microelectromechanical Systems, 22(2)

ISSN
1057-7157

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Publication Date
2013-04-01

DOI
10.1109/jmems.2012.2233719

Peer reviewed

JMEMS Letters

Sputtered–Anodized Ta_2O_5 as the Dielectric Layer for Electrowetting-on-Dielectric

Lian-Xin Huang, Bonhye Koo, and Chang-Jin "CJ" Kim

***Abstract*—Evaluating the anodized tantalum pentoxide (Ta_2O_5) that has been recently reported as a dielectric for low-voltage electrowetting-on-dielectric (EWOD) devices, we find a severe deterioration in performance if the working liquid is actuated with positive dc voltage. In an effort to reduce the limitation of this otherwise attractive dielectric material for EWOD, proposed herein is a Ta_2O_5 layer prepared by anodizing a sputtered Ta_2O_5 film. This sputtered–anodized Ta_2O_5 allows the use of positive dc signals, while maintaining the low-voltage actuation for which the anodized Ta_2O_5 was originally introduced. All the EWOD tests were performed with a conductive liquid droplet in an air environment. [2012-0254]**

***Index Terms*—Dielectric, electrowetting, electrowetting-on-dielectric (EWOD), tantalum pentoxide.**

I. Introduction

Performance and reliability of electrowetting-on-dielectric (EWOD) devices heavily depends on dielectric material [1]–[5]. The common dielectric materials (e.g., silicon dioxide, Parylene, and silicon nitride) are chosen for their reliability under EWOD actuation, despite their relatively low dielectric constants (3 to 4), resulting in relatively high actuation voltage (70–100 V for $\sim$1-μm-thick dielectric). Several high-κ materials (e.g., barium strontium titanate) have been confirmed to lower actuation voltage [6] but did not provide the film quality that is more critical in practice. Furthermore, once reasonably high, voltage-reducing benefits of increasing dielectric constant diminish due to an additional low-κ dielectric layer (e.g., Teflon or Cytop) used as a hydrophobic topcoat.

Tantalum pentoxide (Ta_2O_5), with a relatively high dielectric constant (i.e., 18.5–27.5 [7], [8]), has been recently reported as an attractive material to reduce the operation voltage of EWOD [9]. Anodized Ta_2O_5 is particularly compelling because of its low-temperature fabrication and good film quality (e.g., negligible pinholes). However, anodized Ta_2O_5 EWOD devices are found to suffer from severe deterioration in performance if positive dc or relatively high-frequency ac is applied to the working liquid, as preliminarily reported in [10], limiting its usage only to negatively biased dc and relatively low-frequency (< 100 Hz) applications.

Auspiciously, anodization of a sputtered Ta_2O_5 rather than a Ta metal has been reported to provide high-performance capacitors that are insensitive to polarities [11]. This promising result suggests a path to overcome the severe discrepancy between polarities ($\pm$dc) encountered when using the anodized Ta_2O_5 for EWOD devices. To assess Ta_2O_5 as a high-κ dielectric material for low-voltage EWOD, this letter first identifies the limitations of anodized Ta_2O_5 by voltage type and comparatively evaluates three types of Ta_2O_5 categorized by its fabrication methods: sputtered, anodized, and sputtered–anodized.

Manuscript received September 7, 2012; revised November 10, 2012; accepted November 25, 2012. Date of publication January 8, 2013; date of current version March 29, 2013. Subject Editor H. Jiang.

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Digital Object Identifier 10.1109/JMEMS.2012.2233719

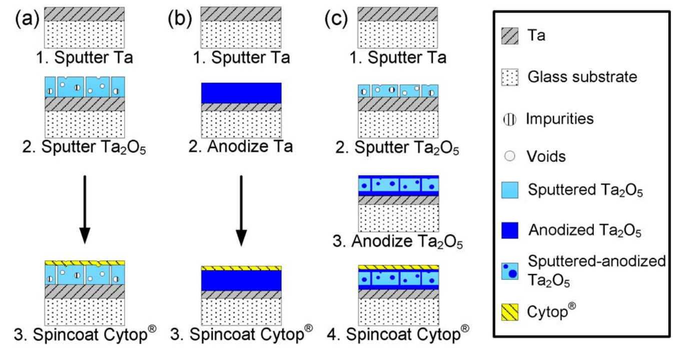

Fig. 1. Process flow to prepare (a) sputtered, (b) anodized, and (c) sputtered–anodized Ta_2O_5 EWOD devices.

II. Device and Experiments

A. Fabrication of Ta_2O_5 Films

Process flows to fabricate EWOD test devices with the three types of Ta_2O_5 are shown in Fig. 1. For all three types, the process started by sputtering a 375-nm-thick Ta contact electrode on glass slides.

Sputtered Ta_2O_5: As shown in Fig. 1(a), a 200-nm Ta_2O_5 film was sputtered on the Ta electrode in O_2 and Ar mixture (1 : 4) at 5-mtorr operating pressure. The film had some impurities (e.g., Ta metal particles) and voids (or pinholes).

Anodized Ta_2O_5: As depicted in Fig. 1(b), a Ta_2O_5 film was grown by anodizing the Ta electrode in 0.01 wt% citric acid electrolyte at room temperature while using a platinum sheet as the counter electrode [12], [13]. First, a constant current density of 0.8 mA/cm^2 was applied by a power source (Keithley Model 2425) until the measured voltage reached 100 V. The increase in voltage indicates growth of the anodized Ta_2O_5 film. Second, a constant voltage of 100 V (with variable current) was applied by the same power source for 1 h. The constant-current mode was used to make sure that the anodic film grew with a fixed value of anodization constant [12] (i.e., 20 Å/V), and the constant-voltage mode was subsequently used to obtain the final desired film thickness [13]. The anodic oxide growth initiates at the metal–electrolyte interface and continues to grow at both metal–oxide and oxide–electrolyte interfaces as oxide evolves [14].

Sputtered–anodized Ta_2O_5: As illustrated in Fig. 1(c), a Ta_2O_5 film was formed by combining the above two processes. A Ta_2O_5 film was first deposited on Ta by dc sputtering for 461 s, resulting in a 180-nm-thick layer. The sputtered Ta_2O_5 was then anodized until the thickness reached 200 nm. The conditions of sputtering and anodizing for the sputtered–anodized Ta_2O_5 were the same as those of the individual sputtering and anodization processes mentioned above. During anodization of the sputtered Ta_2O_5, a film of anodized Ta_2O_5 was formed both on top and at the bottom of the sputtered Ta_2O_5 [13], [14], as shown in step 3. In addition, the voids in the sputtered Ta_2O_5 were filled, and the metal impurities were oxidized, resulting in densification of the sputtered Ta_2O_5 [11]. Hence, the quality of the Ta_2O_5 film was expected to significantly improve.

After Ta_2O_5 formation, their film thicknesses were measured by NanoSpec using a refractive index of 2.22 [7] and confirmed by Dektak

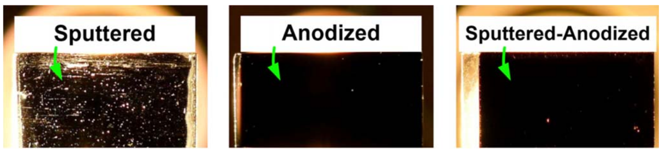

Fig. 2. Results of pinhole test for the three types of Ta_2O_5 films.

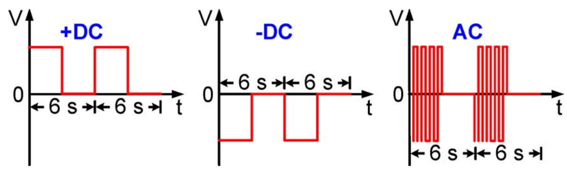

Fig. 3. Actuation signals for electrowetting testing.

6 profilometer. The last fabrication step for all three devices was the addition of a 50-nm hydrophobic Cytop coating. After spin coating, the film was baked at 150 °C on a hotplate for 10 min to remove the solvent and then baked at 195 °C for 1 h to anneal.

B. Pinhole Testing of Ta_2O_5 Films

One of the most common failure mechanisms of EWOD devices is current leakage across the dielectric (and the resulting electrolysis on the surface contacting the liquid), which may be exacerbated by pinholes in the dielectric layer. The quality of the prepared Ta_2O_5 films was evaluated by revealing the presence of pinholes. When a sample was placed in an etchant that selectively etches Ta [15], [16], the Ta under the pinholes in Ta_2O_5 was etched away, allowing light to pass through them and the glass substrate beneath. To prepare the etchant, 20 mL of 16% NaOH solution was first heated to 85 °C, and then, 10 mL of 30% H_2O_2 solution was slowly added. When an EWOD sample without Cytop top coating was placed in the etchant, numerous bubbles were instantly generated on the region of fully exposed Ta (i.e., not covered by Ta_2O_5 at all), indicating Ta etching. After 10 min of etching, the fully exposed Ta was removed; after 30 min, the Ta under the pinholes was also removed.

A light source and a digital camera were placed at the Ta_2O_5 side and glass side of the test samples, respectively. Light traveled through the pinholes in Ta_2O_5, the etched holes in Ta, and the glass substrate to the camera. Observed results of pinhole distribution in the three types of Ta_2O_5 films are shown in Fig. 2. The pinhole density of the sputtered Ta_2O_5 film was much higher than that of the anodized one. The pinhole density of the sputtered–anodized Ta_2O_5 film was comparable to the anodized Ta_2O_5 film, clearly showing that the additional anodization step improved the film quality by reducing the pinhole density of the sputtered Ta_2O_5.

C. EWOD Experiments

The liquid droplet used for EWOD tests consists of glycerin and KCl standard solution (Fluka, $\sigma = 0.1413$ S/m) in a volume ratio of 1 : 1. The conductivity of the resulting mixture (0.013 S/m) was high enough to ensure that the voltage drop mainly occurred across the hydrophobic and dielectric layers. Use of glycerin prevented evaporation of the droplet throughout the experiments. The actuation signals for the electrowetting testing with +dc, −dc, and ac square wave are shown in Fig. 3. Voltage is on for 3 s and off for 3 s in each cycle. At every half actuation cycle, an image of the droplet was captured by a charge-coupled device camera (PixeLINK) and analyzed by a contact-angle measurement program.

To test the polarity effect, +dc and −dc were used. Positive potential applied to the droplet is denoted as +dc; the electrode (Ta) below the dielectric (Ta_2O_5) is always grounded. To test the frequency effect, an ac square wave with frequencies ranging from 50 Hz to 1 kHz was used. The amplitude values of dc and ac (RMS value) were both 13 V, which corresponds to an electrowetting number $Ew = 0.31$ for the given dielectric materials and their thicknesses. Modified from the Lippmann–Young equation [6] for the current sample, (1) defines Ew as a nondimensionalized measure of the electrowetting effect of EWOD surfaces. A larger value of Ew corresponds to a stronger electrowetting effect and usually more contact-angle reduction. Thus,

$$\cos\theta_V - \cos\theta_0 = Ew = \frac{\varepsilon_0 \varepsilon_r \varepsilon_{\mathrm{Cytop}}}{2\gamma(\varepsilon_r t_{\mathrm{Cytop}} + \varepsilon_{\mathrm{Cytop}} t_r)} V^2 \tag{1}$$

where γ is the surface tension of the liquid–gas interface; ε_0 is the vacuum permittivity; θ_V and θ_0 are contact angles with and without voltage, respectively; $\varepsilon_{\mathrm{Cytop}}$ and ε_r are the dielectric constants of Cytop and Ta_2O_5, respectively; t_{Cytop} and t_r are the thicknesses of Cytop and Ta_2O_5, respectively; and V is the voltage across Ta_2O_5 and Cytop layers together.

III. Results and Discussion

The EWOD experiments were carried out for 500 actuation cycles (i.e., 50 min), using all three types of Ta_2O_5. The initial contact angle with no voltage applied (V_{off}) was 103°. We report EWOD performance in terms of its resultant contact-angle reduction; the greater the reduction, the better the EWOD performance. Each data point in Fig. 4 is an average of four repeated experimental results. In addition to the Ta_2O_5 films, we also tested thermally grown SiO_2 as a reference dielectric material for its known quality and to compare to other studies. In order to maintain the same electrowetting number (Ew), a signal with an amplitude of 30 V was applied on the SiO_2 device, comprised of 560-nm SiO_2 and 50-nm Cytop. The performance of SiO_2 is presented as curve fits to keep the Ta_2O_5 data discernible.

A. DC Actuation

The EWOD performance with dc actuation is shown in Fig. 4(a). For the sputtered Ta_2O_5 under −dc, the contact angle reduced more than for the other two types, and even SiO_2. We speculate that this interesting result was related to the self-healing effect [3]: The Ta exposed under the many pinholes was anodized during the −dc actuation to form a thin layer of Ta_2O_5. While the general thickness of the sputtered Ta_2O_5 film was measured at 200 nm, the anodic Ta_2O_5 grown at the bottom of the self-healed pinholes is locally much thinner ($\leq$ 26 nm), making the actual overall capacitance larger than that calculated based on the nominal thickness of 200 nm. Accordingly, the actual electrowetting number of the sputtered (and then self-healed) Ta_2O_5 was larger than intended, resulting in a comparatively larger contact-angle reduction. On the other hand, when +dc potential was applied to the droplet, electrowetting failed due to severe electrolysis; no data could even be collected. Note that there is no self-healing process when the droplet is positively biased.

For the anodized Ta_2O_5 under −dc, very good EWOD performance was obtained, confirming the result of [9]. However, this strong EWOD performance was again limited to negatively biased actuation only [10]. Under +dc, as in the case of sputtered Ta_2O_5, no data could be collected due to severe electrolysis. The diode-like behavior of the Ta-anodized-Ta_2O_5 capacitors was the main reason for electrolysis in these anodized Ta_2O_5 devices.

For the sputtered–anodized Ta_2O_5, not only was the EWOD performance equal to that of the anodized Ta_2O_5 under −dc, but a healthy electrowetting effect was observed under +dc as well. Although positive charges are continuously generated and trapped near the Ta-anodized-Ta_2O_5 interface under +dc, the degradation is very slow [11]. As a result, electrolysis did not occur until after 380 cycles—long enough to complete tasks in many EWOD applications. This result of the sputtered–anodized Ta_2O_5 with +dc actuation is in stark contrast with the immediate electrolysis suffered by both the sputtered and anodized Ta_2O_5. In sum, the sputtered–anodized Ta_2O_5 exhibited EWOD performance comparable to the thermal SiO_2 (one of the

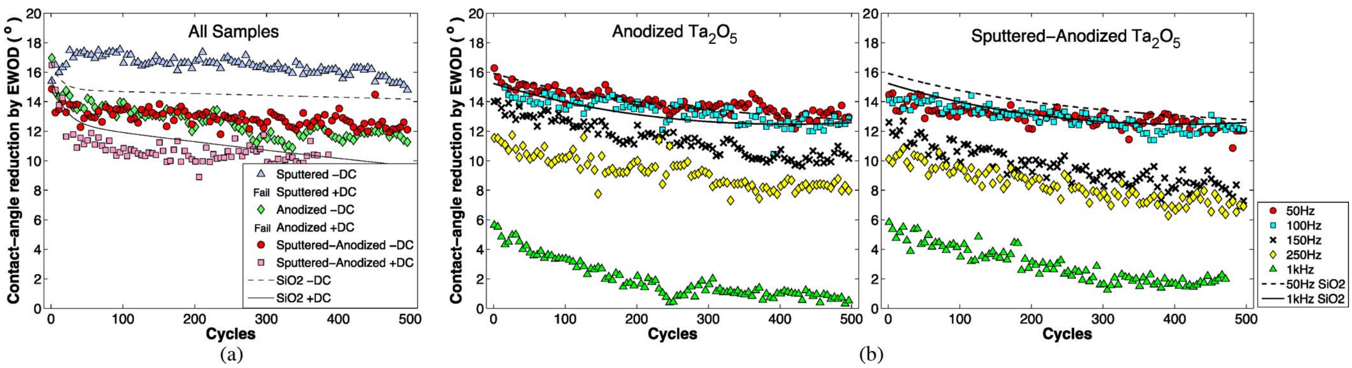

Fig. 4. Electrowetting-induced contact-angle reduction measured on EWOD devices under (a) dc actuation and (b) ac actuation. The performance of thermal SiO_2 [10] is included as a high-standard reference after an exponential curve fitting of the experimental data.

TABLE I
COMPARISON OF Ta_2O_5 AND SiO_2 FILMS

Type of dielectric	*Pinholes*	*AC actuation*	*+DC actuation*	*-DC actuation*
Sputtered Ta_2O_5	Many	Failed	Failed	Excellent
Anodized Ta_2O_5	Negligible	Deteriorated for >100 Hz	Failed	Very good
Sputtered-anodized Ta_2O_5	***Negligible***	Deteriorated for >100 Hz	***Good***	***Very good***
Thermal SiO_2	Negligible	Excellent	Good	Very good

most reliable dielectrics for EWOD) for up to 380 actuation cycles, overcoming the polarity dependence of Ta_2O_5 for short-term EWOD operation.

B. AC Actuation

The EWOD performance with ac actuation is shown in Fig. 4(b). For the sputtered Ta_2O_5, electrowetting failed with electrolysis occurring at any frequency; no data could be collected. For the anodized Ta_2O_5, the EWOD performance deteriorated as the actuation frequency increased, revealing a strong frequency effect. For the sputtered–anodized Ta_2O_5, we observed frequency dependence similar to that of the anodized Ta_2O_5. In comparison, the thermal SiO_2 revealed little frequency dependence, as shown by the curve fits in both figures. In summary, a low frequency signal ($\leq$ 100 Hz) or an imposed negative bias (if acceptable) should be used, when one needs to use either the anodized or the sputtered–anodized Ta_2O_5 layer as an EWOD dielectric material with ac actuation.

IV. SUMMARY AND CONCLUSION

Table I summarizes the observations of experimental results. Sputtered Ta_2O_5 exhibited the least desirable dielectric properties for EWOD, all things considered: poor film quality (e.g., many pinholes) and strong polarity and frequency dependence values, failing under both positively biased dc and ac actuation. Anodized Ta_2O_5 has negligible pinholes and exhibited good dielectric properties for EWOD but only under negatively biased actuation. For ac actuation, signals above 100 Hz are to be avoided. The sputtered–anodized Ta_2O_5 inherited good film quality and marginal frequency dependence from the anodized Ta_2O_5, but the main advantage of the sputtered–anodized Ta_2O_5 is its ability to allow +dc actuation, showing EWOD performance comparable to thermal SiO_2 for short-term operations (e.g., < 380 cycles).

In conclusion, a combination of sputtered and anodized Ta_2O_5 allowed a dc application of positive bias (i.e., +dc actuation), in contrast to the sputtered or anodized Ta_2O_5 alone, which failed under any positively biased dc signal (i.e., +dc actuation). All three types of Ta_2O_5 were successful for −dc actuation. For ac actuations, on the other hand, the sputtered–anodized Ta_2O_5 and the anodized Ta_2O_5 performed similarly well, whereas sputtered Ta_2O_5 failed.

ACKNOWLEDGMENT

The authors would like to thank T. Liu for helpful discussions and J. Jenkins and A. Lee for manuscript preparation.

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