Characteristics of Electrowetting of Self-assembled Monolayer and Z-Tetraol Film

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A study of electrowetting using an Octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) and Z-Tetraol 2000 perfluoro-polyether lubricant as hydrophobic layers on Si and SiO$_2$ wafer was performed. The SiO$_2$ layer used as insulating layer was thermally grown on the silicon wafer to a thickness of 220-230 nm. The results demonstrated that the contact angle decreased from 100° to 80° at 28 V applied potential on SiO$_2$ wafer coated with OTS and the contact angle appeared to be reversible. However, the contact angle on the SiO$_2$ wafer coated with Z-Tetraol 2000 was not observable at 28 V applied potential. Furthermore, the contact angle on the Si wafer coated with OTS or Z-Tetraol 2000 appeared to be irreversible due to the generation of electrolysis in the droplet. It is concluded that it is feasible to use SAM as a hydrophobic layer in electrowetting applications.

1. Introduction

Electrowetting is a relatively new method to attain a driving force for moving a droplet used in microfluidic devices, such as lab-on-a-chip and MEMS. In the electrowetting setup, the contact angle of a droplet on the surface can be manipulated by applying an electric field between the droplet and the counter electrode underneath the droplet. The general experimental schematic for electrowetting is shown in Fig. 1. The cathodal electrode is inserted into the droplet and the anodal electrode is contacted with the Si substrate. When an external electric field potential is applied, the charges and dipoles can redistribute and modify the surface energy at the interface. This in turn, varies the wettability of surface. The insulating layer covering the base electrode blocks the electron transfer, which accumulates a high surface charge density on the surface. The insulating layers used include parylene, silicon dioxide, and barium strontium titanate (BST). The hydrophobic layer, such as amorphous fluoropolymer, coated on the insulating layer is to attain a large contact angle. Electrowetting phenomenon has been used to transport, merge, and create a liquid droplet in microfluidic circuits.[1]

In many literatures,[2-5] the relationship between the contact angle θ_V of the droplet and applied potential V was described according to the Lippmann-Young equation. In the Eq. (1), the solid-liquid interfacial tension, γ_{SL}, is related to the electric potential across the droplet.

$$\gamma_{SL} = \gamma_0 - \frac{1}{2} C V^2$$

(1)

where γ_0 is the solid-liquid interfacial tension when the external electric potential V is zero and C is the capacitance of the dielectric layer. The mechanical equilibrium of the three interfacial tensions (Fig. 2) is expressed by Young's equation as follows:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

(2)

where γ_{SV} is the solid-vapor interfacial tension, γ_{SL} is the solid-liquid interfacial tension, and γ_{LV} is the liquid-vapor interfacial tension. Assuming C=$\varepsilon_0\varepsilon$/d (ε_0 is the vacuum permittivity, ε is the dielectric constant of the insulating layer, and d is the thickness of the insulating layer), the relationship between the contact angle and the applied potential is expressed by incorporating Eq.(1) into Eq.(2):

$$\cos\theta = \cos\theta_0 + \frac{1}{2}\frac{\varepsilon\varepsilon_0}{\gamma_{LV}d}V^2$$

(3)

where θ_0 is the contact angle when the applied potential is zero. In Lippmann-Young equation, the surface tensions of liquid–vapor and solid–vapor are unaffected by the electric field, and the observed change in the contact angle is due to the decrease in the surface tension of solid–liquid interface. However, Lippmann-Young equation only qualitatively explains the observed change in the
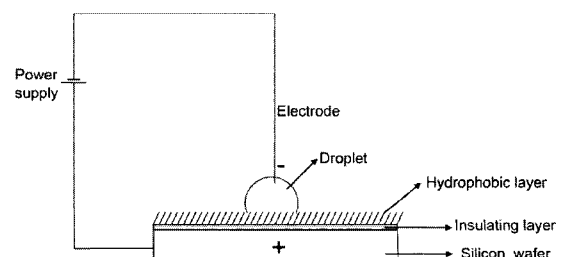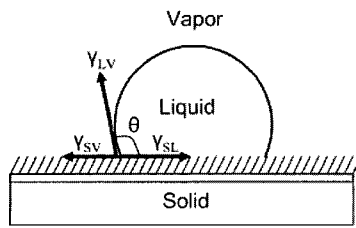

Fig. 1 Schematic of electrowetting setup

Fig. 2 The mechanical equilibrium of a droplet on a solid surface according the Young's equation

contact angle with the applied potential. The charge trapping effect and the redistribution of the charge on the three-phase contact line are not considered in this equation.[5-6]
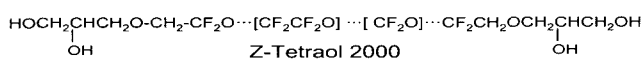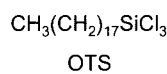
Moon[2] et al investigated the thickness of the hydrophobic layer as function of the applied potential to create 15° modulation of contact angle. The work showed that decreasing the thickness of the hydrophobic layer can decrease the required potential; however, a very thin hydrophobic layer can lead to electrolysis generation.

Self-assembled monolyer (SAM), which is an ultrathin organic film, has been used to modify the surface properties due to its good bonding strength and hydrophobic properties. Octadedyltrichloro-silane (OTS), which is one of alkylsilane SAM, can be readily coated on Si surface. The contact angle on the OTS coated Si wafer was 100° and the thickness of OTS was 2.8 nm.[7] Z-Tetraol 2000 is one of the perfluoropolyether lubricants that are used for the hard disk-drive for low frictional properties.[8] The hydroxyl group on the main chain of perfluoropolyether can react with either Si–OH or Si–H group on the silicon surface.[9] It was reported that alkanethiol SAM coated on gold was previously used in electrowetting. However, the contact angle was irreversible at the operating potential due to the dielectric breakdown and desorption of SAM.[2-3]

In this paper, OTS and Z-Tetraol 2000 were coated on SiO$_2$ and Si wafers to investigate their electrowetting properties. The 220-230 nm thick SiO$_2$ layer was thermally grown on SiO$_2$ wafer to function as the main insulating layer. SAM and Z-Tetraol 2000 on Si wafer work as a hydrophobic and insulating layer. The reversibility of contact angle under the applied potential and the required potential were observed. The contact angle kinetics was inverstigated when the operating potential was gradually increased or alternately applied. Another motivation of this work was to assess the feasibility of using SAM and Z-Tetraol film in electrowetting applications.

2. Experiment

OTS SAM and Z-Tetraol 2000 were used as hydrophobic layers on the substrate. The chemical formulae of OTS and Z-Tetraol 2000 are shown below. OTS was coated on Si and SiO$_2$ wafer according to methods suggested in a previously published literature.[6] Si and SiO$_2$ wafer were first cleaned and then hydroxylated in piranha solution (H$_2$SO$_4$:H$_2$O$_2$ = 7:3, v:v) for 20 min at 80 $^\circ$C. The OTS coating was prepared by immersing the hydroxylated Si and SiO$_2$ specimens in a 1mM OTS–toluene solution for one hour at room temperature.

$$CH_3(CH_2)_{17}SiCl_3$$

OTS

$$HOCH_2CHCH_2O\text{-}CH_2\text{-}CF_2O\cdots[CF_2CF_2O]\cdots[CF_2O]\cdots CF_2CH_2OCH_2CHCH_2OH$$
$$\quad\quad\;\; |\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad OH\quad\quad\quad\quad Z\text{-}Tetraol\ 2000\quad\quad\quad\quad\quad\quad OH$$

Z-Tetraol 2000 was coated on Si and SiO$_2$ wafer by using a dip-coating procedure. A 0.2 wt% solution of Z-Tetraol 2000 in Vertrel-XF solvent was prepared. The wafers were dipped into the solution at a speed of 30mm/min. The wafers were immersed for 1min and then withdrawn at the same speed. Finally, the coated wafers were heated at 120 $^\circ$C for 2 hours.

Si wafer was mainly used as the substrate. The silicon dioxide layer was thermally grown on the silicon wafer to a thickness of 220-230 nm. The experimental setup used is shown in Fig. 1. A drop of deionized water (~5μL) was dropped on the surface. The metal microwire (about 100μm in diameter), which functions as the cathodal electrode, was inserted into the droplet. The Si substrate was contacted to positive potential as the anodal electrode. A controllable DC power supply was used in the experiment. The contact angle was observed by optical microscopy equipped with a CCD camera. The measurement of contact angle was carried out at a temperature of 25 $^\circ$C and a relative humidity of 52%. A fresh droplet was used in each contact measurement to avoid the effect of evaporation. The contact angle measurement was repeated for 5 times and an average value was taken.

3. Results and discussion

3.1 Electrowetting on Si wafer coated with OTS SAM and Z-Tetraol 2000

Compared with 30° of contact angle on hydroxylated Si wafer, the contact angle on the OTS SAM coated Si wafer was 100°. It indicated that Si surface became hydrophobic and OTS SAM could be successfully coated on the Si surface. When SAM was coated on the Si wafer, the SAM functioned as a hydrophobic and insulating layer in the electrowetting experiment. When the applied potential was increased up to 3 V, there were air bubbles generated around the cathodal electrode, which are shown in Fig. 3a. It indicated that the dielectric layer broke down and the electrolysis occurred when the potential reached 3 V. However, the contact angle did not change observably until the electrolysis occurred. It was found that even though the contact angle could be decreased with increasing potential, the contact angle appeared to be irreversible at these operating potentials because of degradation of the SAM by desorption.

The contact angle on the Z-Tetraol 2000 coated Si wafer was about 90°. Also, it can be observed from Fig. 3b that the bubbles generated around the cathodal electrode when 3 V potential was applied.
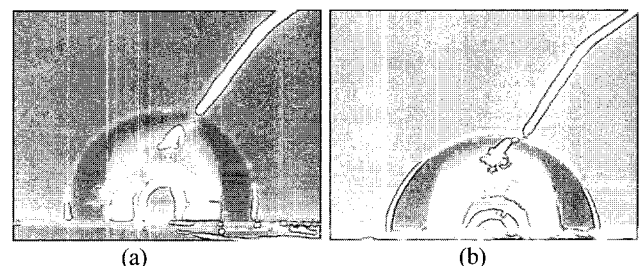

(a)   (b)

Fig. 3 Bubbling effect around the cathode electrode at 3 V applied potential for (a) OTS SAM coated Si wafer and (b) Z-Tetraol 2000 coated Si wafer

3.2 Electrowetting on SiO$_2$ wafer coated with OTS SAM and Z-Tetraol 2000

Fig. 4 shows the contact angle with respect to different applied potentials. The contact angle was 100° at the initial state corresponding to 0 V potential. The contact angle was 95° while the potential was turned off. In the electrowetting experiments, the threshold voltage is the potential at which the contact angle changes

(a)   (b)   (c)
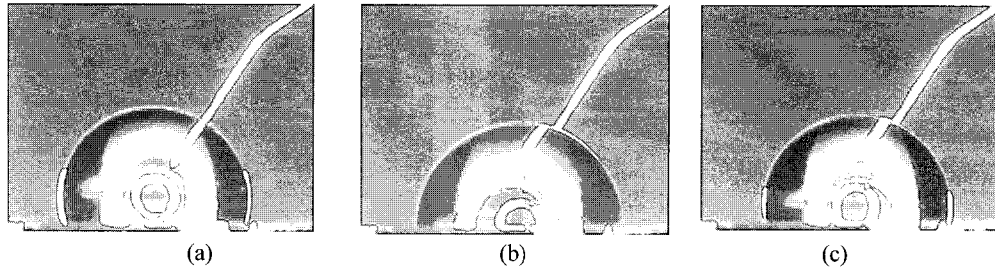
Fig. 5 Images of contact angle kinetics (a) Initial state; (b) At 28 V applied potential; (c) Off state

observably. From Fig. 4, it can be seen that when 20 V potential was applied, the contact angle decreased from 100° to 90°. The change of contact angle under 16 V potential was not significant. It was thought that the threshold voltage was about 20 V. When 28 V potential was applied, the contact angle was reduced from 100° to 80°.
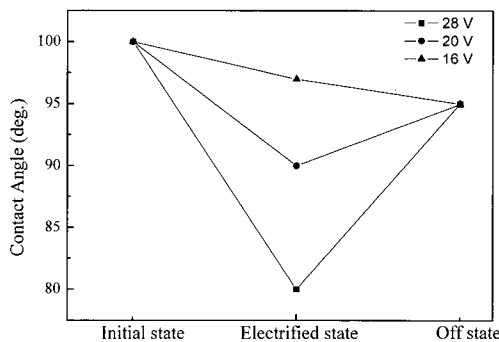

Fig. 4 The contact angle on the SAM coated SiO_2 wafer with respect to different applied potentials

The dielectric layer of SiO_2 on Si substrate blocks the electron transfer, accumulating a high electric field across the water droplet and resulting in an increase of surface charge density on the substrate. According to the Lippmann-Young equation, the change of contact angle can be increased by increasing the applied potential. However, Moon[2] et al observed that contact angle was saturated at ~ 80° on SiO_2 insulating layer coated with a Teflon hydrophobic layer.[1-2] The reason for the saturation phenomenon is not yet understood. Verheijen[5] et al suggested that the saturation phenomenon was due to the trapped charge in the insulating layer. The other explanation for contact angle saturation by Seyrat[10] is related to the material deficiency.

As known, the movement of a stream of water can be deviated by an electrostatic source due to the alignment of water dipole along the electric field.[11] Also, it was proposed that the water droplet consists of water clusters that have equal hydrogen bonding in all directions. The water clusters are arranged randomly and bonded to each other with hydrogen-bonding network.[12-13] The electric field results in the breakage of some hydrogen-bonding network, which is the reason why the electric field acts on the water dipole to reorient it along the electric field direction.[14-15] This implies that the breakage of hydrogen-bonding network in water clusters resulted in the decrease of the contact angle.

When the potential was turned off, the surface charge density returned to the original state. The hydrogen-bonding network in the water droplet was built up again and the contact angle increased to 95°. It was found that the contact angle was reversible at the operating potential. The decrease of 5° of contact angle was due to the surface roughness or heterogeneity.[4] The contact angle kinetics is shown in Fig. 5 for the case when a 28 V applied potential is turned on and then turned off.

In Fig. 6, when the potential was increased gradually from 0 V to

28 V over 4 minutes, the contact angle with respect to the increased potential decreased from 100° to 93°. Compared with the modulation of 20° when the potential was applied discretely, only 7° was modulated under 28 V potential when the potential was increased gradually. This observation suggested that the hydrogen-bonding network can remain intact under a low electric field. With the gradual increase of applied potential, the electric field is lowered by trapping of the charge, which leads to the decrease of electrowetting force,[5] so the modulation of contact angle is small at the applied potential.
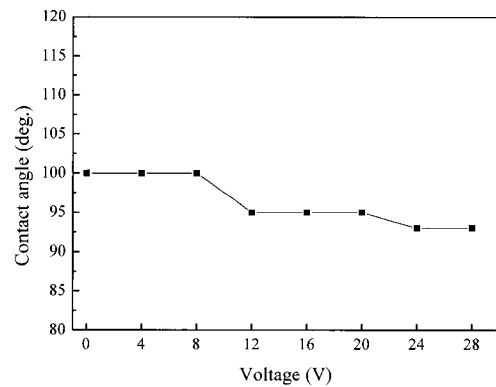

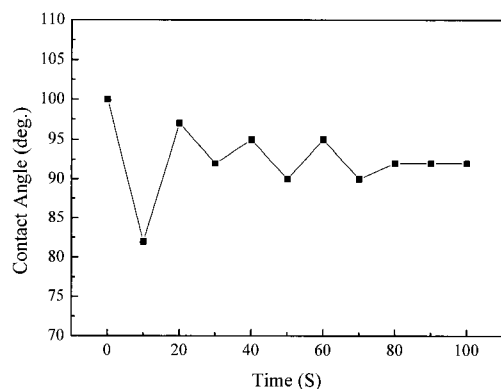Fig. 6 The contact angle kinetics with respect to gradually increasing applied potential

Fig. 7 The contact angle kinetics with respect to time, when the applied potential was alternately applied from 0 V to 28 V every 10 seconds

In Fig. 7, when the potential was applied alternately from 0 V to 28 V every 10 seconds, it was found that the change in contact angle became insignificant after about 3 cycles. The results further implied that the electric field across the droplet decreased with operational time due to the trapping of charges.

In the electrowetting experiment of Z-Tetraol 2000, it was found that the contact angle did not change observably even though 28 V potential was applied. As known, there are hydroxyl groups bonded

on the main chains of Z-Tetraol 2000 molecules. The possible interpretation is that the bonding interaction between the water molecules and hydroxyl groups improves the interfacial tension which resists the wetting on the substrate in the electric field, and thus there was no observable decrease in the contact angle at the operating potential.

4. Conclusions

Electrowetting characteristics of OTS SAM and Z-Tetraol 2000 coated on Si and SiO_2 wafer were investigated in this work. Experimental results showed that when OTS SAM was coated on the SiO_2 wafer, the contact angle decreased from $100°$ to $80°$ at 28 V applied potential and the contact angle was reversible at this operating potential. Electrowetting on SAM coated on SiO_2 wafer suggested a new method for electrowetting application. The contact angle did not change observably until the electrolysis occurred at 3 V applied potential when OTS SAM or Z-Tetraol 2000 was coated on Si wafer. The possible explanation for the change of contact angle in the electric field is due to the breakage of the hydrogen-bonding network in water clusters. The interfacial tension induced by the bonding interaction between the water and Z-Tetraol 2000 is the key factor affecting the change of contact angle.

ACKNOWLEDGEMENT

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