

Hydroxylation of SiO₂ surface and Threshold Voltage Shift of Organic Field Effect Transistors

Chong Lim Chua and Kai Lin Woon*

¹*Low Dimensional Materials Research Center, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia*

**ph7klw76@um.edu.my*

(Received: 1 August 2016; published 23 November 2016)

Abstract. Two methods of SiO₂ substrate cleaning are compared. One method, the SiO₂ surface are intentionally hydroxylated with a mixture of hydrochloric acid and hydrogen peroxide during cleaning, while the other method uses acetone, isopropyl alcohol (IPA) and water to clean the surface sequentially with the aid of ultrasonic agitation. A super-hydrophilic surface with contact angle less than 10° is obtained by intentionally hydroxylating the surface. The contact angles for both surfaces after the phenyltrichlorosilane (PTCS) treatment increased significantly to more than 75°. The hole mobility of these devices are $3 \times 10^{-3} \text{ cm}^2/\text{Vs}$. However, the transfer characteristics of the organic field effect transistor (OFET) over time are drastically different. Intentionally hydroxylating the SiO₂ surface yields very little shift of threshold voltages (less than 5 V) over 4 weeks. The OFET characteristics for the organic solvent cleaned SiO₂ surface disappeared after a week. It seems that hydroxylating the SiO₂ surface before application of PTCS significantly prolongs the lifetime of the OFET devices.

Keywords: Reliability, OFET, SAM, superhydrophilicity

I. INTRODUCTION

Organic field effect transistors (OFETs) have attracted great interests due to the ability to process into large area, flexible, low cost devices^{1,2}. Not only it can be integrated with flexible displays but also can be used for various sensing applications such as temperature, light, gas and biochemical materials for example³⁻⁵. Applications such as biochemical and gas sensing require OFET channels to be exposed in oxygen and moisture rich environment. Exposure the devices in such environments often result in a shift of threshold voltage⁶. In most cases, this is the result of trapped charges either in the organic semiconductor or the gate dielectric or the interface between two layers. The stringent storage requirement of the devices at very low oxygen and moisture levels is hindering applications of OFETs in biochemical and gas sensing environment. Numerous of efforts have been devoted into synthesizing more chemically stable high mobility organic semiconducting materials^{7,8}. Interface between organic semiconductors and dielectric has been shown to significantly influence the shift of the threshold voltages.

One common dielectric is silicon oxide (SiO₂). Hydroxyl (OH) groups are commonly present at the surface of SiO₂. These act as traps during the operation of OFET devices⁹. In order to reduce these traps, a self-assembly monolayer (SAM) is often used to passivate the substrate surfaces. Octadecyltrichlorosilane (OTS), phenyltrichlorosilane (PTCS) and hexamethyldisilane (HMDS) are among the SAM commonly used^{10,11}. These SAMs are able to greatly reduce the surface potential energy and surface trap densities. Although silanization reaction is simple to

carry out, formation of densely packed, high quality, stable self-assembled monolayers are difficult^{12,13}. Many trapping phenomena observed in OFETs with SiO₂ might be related to adsorption of water molecules on the surface of SiO₂ despite the presence of SAMs¹⁴. The lack of precise characterization of SAM on SiO₂ surface further complicates the efforts to find out what process is the best for the formation of densely packed SAMs on the surface.

Here we report that by intentionally hydroxylate the SiO₂ surface with a mixture of hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) before application of SAM, little threshold shift voltage is observed over 4 weeks compared with the device without in the ambient air. The surface with intentional hydroxylation also exhibits superhydrophilicity (contact angle < 10°).

II. EXPERIMENTAL DETAILS

A. Creating Superhydrophilic SiO₂ surface

Two solutions are used: RCA-1 and RCA-2. RCA-1 consists of 1 part of ammonium hydroxide (NH₄OH), 1 part of hydrogen peroxide (H₂O₂) and 5 parts of de-ionized (DI) water (resistivity ~15 MΩ-cm). Firstly, 1 part of NH₄OH is added into 5 parts of DI water. The mixture is heated to ~70 °C. When the temperature is reached, the solution is removed from the hot plate and 1 part of H₂O₂ is added into it. SiO₂ (300 nm) /Si substrate substrates are purchased from Ossila (UK). SiO₂ (300 nm) /Si substrate are then put into the solution and left soaking for 10 minutes. Then it is rinsed with copious of DI water and blow-dried with nitrogen gas. RCA-2 consists of 1 part of hydrochloric acid (HCl), 1 part of hydrogen peroxide (H₂O₂), 5 part of DI water. 1 part of HCl is added into 6 parts of DI water to be heated to 70 °C. Then 1 part of H₂O₂ is added into it. The substrates cleaned by RCA-1 are put into the solution and left soaking for 10 minutes. Then it is rinsed with copious of DI water and blow-dried with nitrogen. The substrate or device made from it will be referred as RCA cleaned.

B. Organic solvent cleaned SiO₂ surface

The substrate is immersed in acetone, IPA, and DI water sequentially with the aid of ultrasonic agitation each for 5 minutes. The substrate is then blow-dried with nitrogen gas. The substrate or device made from it will be referred as IPA cleaned.

C. SAM preparation

The deposition of SAM is as follow: First, PTCS solution is prepared by adding 0.1 ml of PTCS into 9.9 ml toluene to make 1 %v/v PTCS solution. The substrate with oxide layer is then immersed in the PTCS solution and maintained at 60 °C for 120 minutes. Then the substrate is removed and rinsed with fresh toluene and cleaned in IPA for 5 minutes in an ultrasonic bath and rinsed again with DI water sequentially to remove any excessive layer. The rinsing of substrate with fresh toluene is found to be crucial as the unreacted PTCS can cleave the pi-conjugation of semiconducting materials due to high reactivity of organosilane. This will destroy the semiconducting properties of the materials. After purging with dry nitrogen, it is heated on a hot stage at 120 °C to enhance cross linking of the organosilane molecules and bond formation on the surface of SiO₂.

D. Contact angle measurement

KSV Theta Lite Optical Video Contact Angle System is used to measure the water droplet contact angles. A 3 μ l of DI water droplet is dropped onto the substrate. The contact angle of the water droplet is then determined.

E. X-ray diffraction measurement

XRD is carried out to examine the crystallinity of P3HT film on the silanized SiO₂ surface. XRD patterns of the films are obtained using Empyrean X-ray diffractometer (PANalytical) with Cu K α radiation of 0.154 nm wavelength. The diffraction data is recorded at 2θ angle of 2° to 25°, with resolution of 0.05°.

F. Device fabrication and Measurement

To fabricate the device, regionregular-P3HT (purchased from American Dye Inc) is dissolved in trichlorobenzene (TCB) to make 15 mg/ml solution. It is stirred and heated at elevated temperature for the material to completely dissolve. It is then dispensed through a 45 μ m diameter pore size filter and spin-coated at 1800 rpm for 3 minutes to give 40 nm thick P3HT. It is then annealed on a hotplate at 120 °C for 15 minutes prior to Gold (Au) (80 nm) Source-Drain electrode deposition to give a channel width of 40 μ m . Two Keithley 236 source-measurement units (SMUs) are used to bias the device and measure the current, where one unit of the SMUs is used to set the source–drain voltage V_{ds} and measure the drain current I_{ds} while another unit of SMU is used to supply the gate voltage V_g and measure the gate current I_g .

III. RESULTS AND DISCUSSIONS

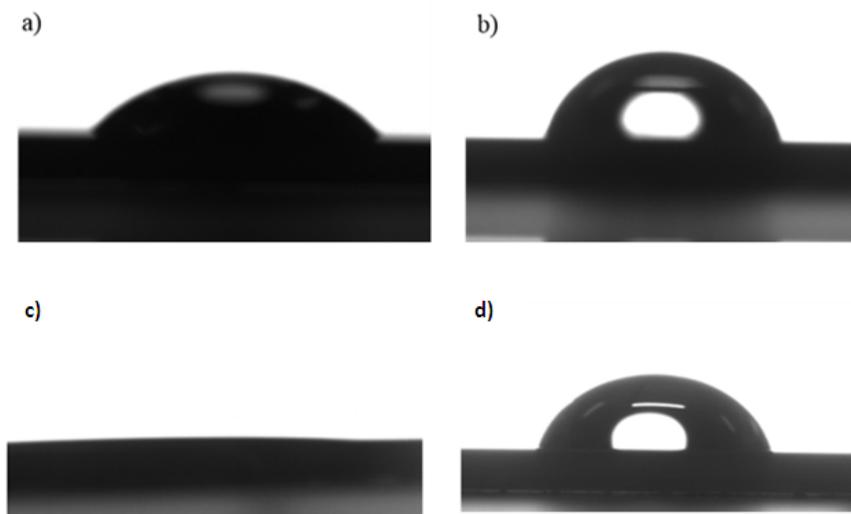


FIGURE 1: The image of a water droplet on (a) IPA cleaned surface, (b) IPA cleaned and PTCS treated surface (c) RCA cleaned surface and (d) RCA cleaned and PTCS treated surface.

Error! Reference source not found.1 shows the images of a water droplet on the IPA and RCA cleaned SiO₂/Si substrates before and after SAM treatments. Before the SAM treatment, the contact angle for IPA cleaned SiO₂ surface is 47° while the contact angle for RCA cleaned SiO₂ surface is too small to be measured ($\theta < 10^\circ$). The very small contact angle indicates that the surface has become highly polar resulting in superhydrophilicity. Superhydrophilicity occurs when the contact angle is too small to be measured. This is because the liquid tends to spread and wet the surface in a larger area. Hence, the contact angle is almost zero. This is only possible when there is a densely packed surface bounded –OH groups at the SiO₂ surface compared with IPA cleaned surface. Both surfaces show a higher hydrophobicity after SAM treatments with contact angle of 80° and 77° for IPA and RCA cleaned SiO₂ surfaces respectively. The drastic increase of contact angle for RCA cleaned SiO₂ surface after SAM treatment indicates the surface bounded –OH groups has fully reacted with PTCS. One would assume that since the contact angles after SAM treatments are almost the same, SAM must have been formed in both surfaces with different cleaning methods. However, due to the different nature of surfaces before SAM treatments, the bonding or the density of bonding with SAM would be different.

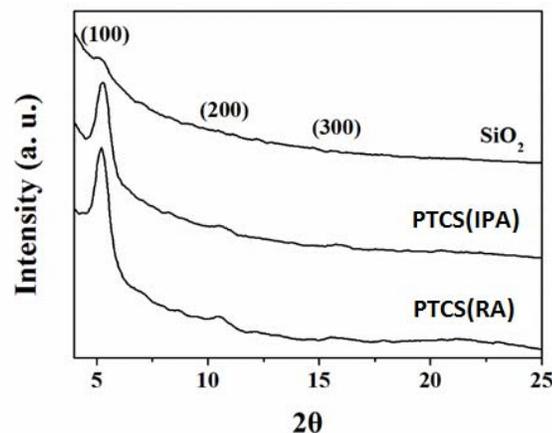


FIGURE 2: X-ray diffraction of P3HT spin coated on pristine SiO₂ and PTCS treated substrate

X-ray diffraction is carried out to examine the crystallinity of regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) film of 40nm thick on the PTCS treated SiO₂ surfaces. Simple treatment of SAM results in improved crystallinity of the thin films. This can be confirmed by the distinct (100) peak of the P3HT thin film on PTCS treated surface at $2\theta = 5.3^\circ$ as shown in **Figure 2**. Not shown here in the Figure 2 is the silicon wafer strong peaks at 35.6° . Without PTCS, the P3HT thin film doesn't show obvious crystalline ordering. The (200) and (300) peaks at $2\theta = 10.5^\circ$ and $2\theta = 16.0^\circ$ respectively indicate a long range order of P3HT on PTCS treated surface. These (200) and (300) peaks are stronger on the substrate cleaned by RCA.

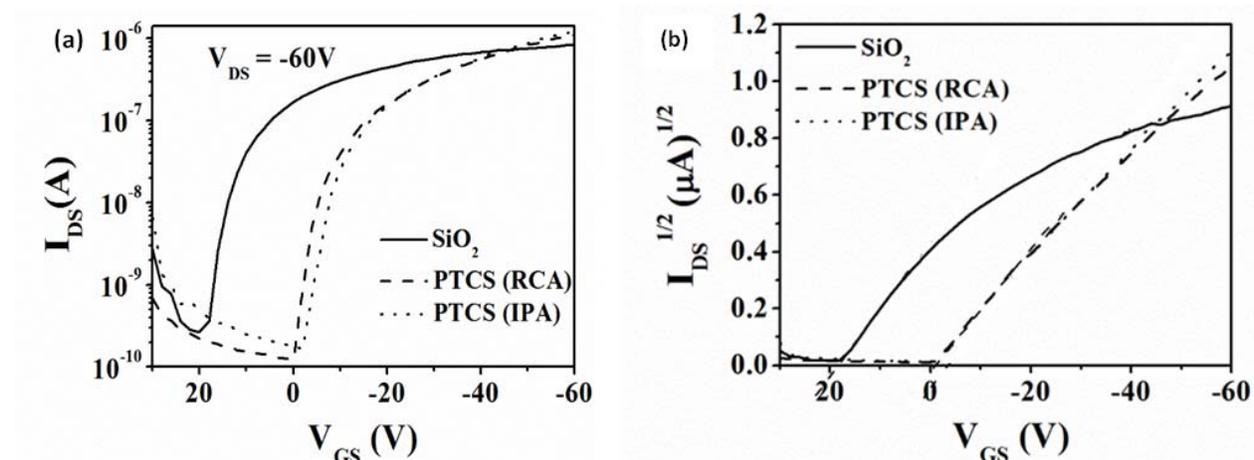


FIGURE Error! No text of specified style in document. (a)Semi-logarithmic curve of transfer characteristic of P3HT based OFET with respect to different substrate treatment (b) Square root curve of transfer characteristic of P3HT based OFET with respect to different substrate treatment

FIGURE Error! No text of specified style in document. (a) and (b) show semi-logarithm curve and square root of I_{DS} against V_{GS} at $V_{DS} = -60$ V respectively. The transfer characteristics are virtually identical for both RCA and IPA cleaned SiO_2 surface. A large positive shift of threshold voltage (~ 18 V) is observed for device without SAM treatment indicating the presence of trapped charges.

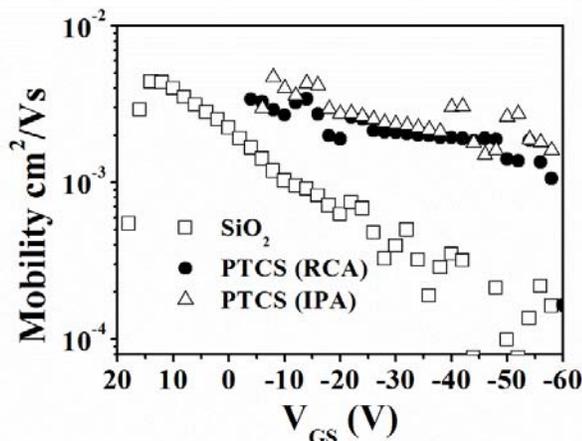


FIGURE 4: Mobility with respect to increasing V_{GS}

FIGURE 4 shows the hole mobility at the linear regime with increasing V_{GS} . The mobilities between SiO_2 -OFET and PTCS treated surfaces are almost the same at and near the threshold voltages. The highest mobility of $2.68 \times 10^{-3} \text{ cm}^2/\text{Vs}$ is obtained from the PTCS(IPA) which is slightly higher than the PTCS(RA) of $2.18 \times 10^{-3} \text{ cm}^2/\text{Vs}$. The mobility of SiO_2 -OFET decreases rapidly as the gate voltage increases. This could be an indication of a bias stress¹⁵. Besides, the SiO_2 -OFET $I_{ON/OFF}$ ratio is more than 3 orders of magnitude ($>10^3$). The gate leakage is more significant without the SAM. On the other hand, PTCS treated SiO_2 substrates show almost identical rate of reduction of mobility over a range of gate voltages tested.

Sub-threshold swing (SS) is the gate voltage swing required to change the drain current by one decade. It is a measure of how easily a transistor can be switched from the off-state to the on-

state and can be related to the density of trap states¹⁶. SS value of 2.44V/decade and 3.15V/decade are obtained for RCA/PTCS-OFET and IPA/PTCS-OFET respectively. The lower SS value for RCA cleaned SiO₂ surface might indicate a better cleaning procedure by RCA and subsequently led to more densely formed SAM. **Table 1** summarizes the key parameters of the devices.

Table 1 OFET performance summary with respect to different substrate treatment.

	Θ (°)	μ (cm ² /Vs)	V_T (V)	V_0 (V)	SS (V/decade)
SiO ₂	N/A	2.64×10^{-3}	18	-18	2.75
PTCS(RCA)	77	2.18×10^{-3}	-1	0	2.44
PTCS(IPA)	80	2.68×10^{-3}	-3	-2	3.15

Although IPA/PTCS-OFET does not exhibit pronounced difference on the transfer characteristics compared to RCA cleaned device, it shows a rapid degradation after a week as depicted in **Figure 5(a)**. The transistor behavior almost disappeared. On the other hand, RCA cleaned device shows very little degradation after even four weeks. For the degradation behavior measurement, the devices are stored in a chamber with concentration of oxygen of about 100 ppm and moisture of about 50 ppm before measurement. It is then taken out for IV measurement every week.

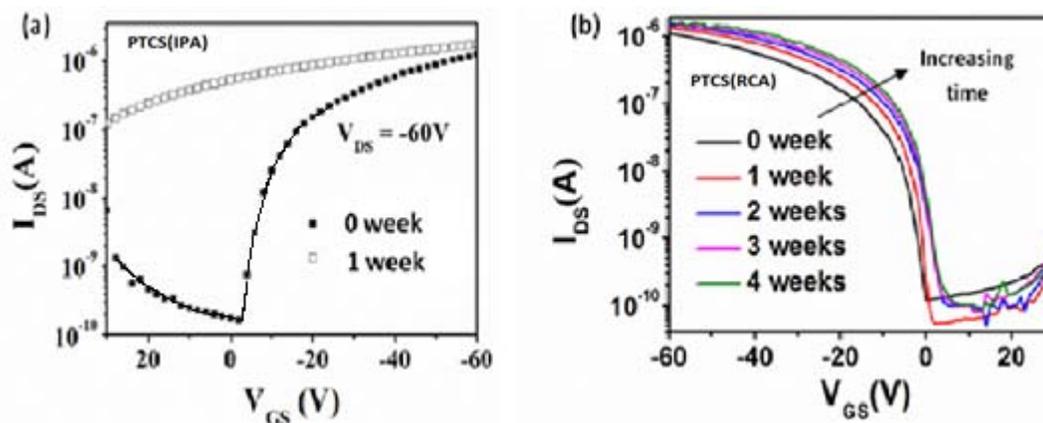


FIGURE 5: Transfer curve of (a) IPA cleaned devices at 0 week and 1 week (b) RCA cleaned device from 0 week to 4 weeks

Figure 5(b) shows that the transfer curves over the 4 weeks. The on-current (I_{ON}) is gradually increased for each measurement after one week for RCA cleaned device. The threshold voltages change from -1.5 V to 2 V over the 4 weeks while the I_{OFF} only increases slightly. The mobility increases from 2.18×10^{-3} cm²/Vs during the first measurement to 4.08×10^{-3} cm²/Vs during the 4th week indicating the possibility of oxygen doping on the P3HT which results in more p-type extrinsic carriers. **Table 2** summarizes the key parameters during the reliability test.

Table 2 Reliability test of OFET.

	μ (cm ² /Vs)	V _T (V)	V ₀ (V)	SS (V/decade)
1st measurement	2.18×10 ⁻³	-1.5	0	2.44
1st week	2.91×10 ⁻³	0	2	1.72
2nd week	3.25×10 ⁻³	1.5	4	2.48
3rd week	3.46×10 ⁻³	1.5	5	2.22
4th week	4.08×10 ⁻³	2	6	2.22

The slow increase of threshold voltage from negative to positive could be the result of the change of polarity of surface trap at the SiO₂/P3HT interface probably due to the slow oxygen doping.

IV. CONCLUSIONS

The reliability of RCA cleaned and IPA cleaned SiO₂ substrates for OFETs have been investigated. RCA cleaned SiO₂ substrates exhibit superhydrophilicity. Despite the fact that the contact angles and the transfer characteristics of the OFETs built using the two different cleaning methods are almost similar, the transfer characteristics changes very different over time. Transfer characteristics of RCA cleaned devices showed more stability over time while the transistor behavior of IPA cleaned device disappears after a week. In order to reduce the degradation of OFET devices using SiO₂ as a dielectric layer, hydroxylating the SiO₂ surface is needed.

Acknowledgements

This work was financially supported by the IPPP Grant (PV120/2012A) and UMRG Grant RP007A-13AFR from the University of Malaya.

-
1. J. W. Ward, Z. A. Lamport and O. D. Jurchescu *ChemPhysChem* **16**, 1118–1132 (2015).
 2. B. Kang, Lee W. H. and Cho K. *ACS Appl. Mater. Interfaces*, **5**, 2302–2315 (2013).
 3. C.W. Chu, S.H. Li, E.H.E. Wu and Y. Yang *Appl. Phys. Lett.* **86**, 253503 (2005).
 4. A. N. Sokolov, B.C.K. Tee, C.J. Bettinger, J.B.H. Tok and Z. N. Bao *Acc. Chem. Res.*, **45**, 361–371 (2012).
 5. S. M. Goetz, C.M. Erlen, H. Grothe, B. Wolf, P Lugli. and G. Scarpa, *Org. Electron.* **10**, 573–580 (2009).
 6. D. Kumaki, T. Umeda and S. Tokito *Appl. Phys. Lett.* **92**, 093309 (2008).
 7. A. Filatre-Furcate, T. Higashino, D. Lorcy and T. Mori, *J. Mater. Chem. C*, **3**, 3569-3573 (2015).
 8. P. Wang, H. Li, C. L. Gu, H. L. Dong, Z. Z. Xu and H. B. Fu *RSC Adv.*, **5**, 19520-19527 (2015).

9. L. L. Chua, J. Zaumseil, J. F. Chang, E. C. W. Ou, P. H. K. Ho, H. Siringhaus and R. H. Friend *Nature* **434**, 194-199 (2005).
10. S. C. Lim, S. H. Kim, J. H. Lee, M. K. Kim, D. J. Kim and T. Zyung, *Synthetic Met.* **148**, 75–79 (2005).
11. J. C. Lin, W. Y. Lee, C. C. Kuo, C. Li, R. Mezzenga and W. C. Chen, *J. Polym. Sci. A Polym. Chem.* **50**, 686–695 (2012).
12. S. P. Pujari, L. Scheres, A. T. M. Marcelis and H. Zuilhof, *Angew. Chem. Int. Ed.* **53**, 6322—6356 (2014).
13. R. H. Tian, O. Seitz, M. Li, W. C. Hu, Y. J. Chabal and J. M. Gao, *Langmuir*, **26**, 4563–4566 (2010).
14. S. G. J. Mathijssen, M. Kemerink, A. Sharma, M. Coelle, P. A. Bobbert R. A. J. Janssen and D. M. de Leeuw, *Adv. Mater.* **20**, 975-979 (2008).
15. T. N. Ng, J. A. Marohn and M. L. Chabinye, *J. Appl. Phys.*, **100**, 084505 (2006).
16. J. H. Bae and Y. Choi *Solid-State Electronics*, **72**, 44-47, (2012).