Study of surface energy of SiO₂ and TiO₂ on charge carrier mobility of rubrene organic field effect transistor

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Abstract- Organic Field Effect Transistors (OFET) find wide applications in large area electronics due to their attractive features such as easy fabrication process, light weight, flexibility and cost effectiveness. Research is directed towards in improving charge carrier mobility since such enhancement would drastically improve OFET device performance. To improve the charge carrier mobility in OFETs, particular attention has been devoted to controlling the surface energy of gate dielectric. In this investigation, silicon dioxide (SiO_2) and titanium dioxide (TiO_2) gate dielectrics with rubrene as organic semiconductor (OSC) has been considered. Modification in gate dielectric has been achieved by OTS-treatment. This paper reports the influence of surface free energy of SiO_2 and TiO_2 gate dielectric on the charge carrier mobility of rubrene OFET. The estimated surface free energy of SiO_2 and TiO_2 is compared with that of the surface free energy of OTS treated SiO_2 and TiO_2. The charge carrier mobility is observed to be increased from when SiO_2 dielectric surface energy was decreased after OTS-treatment. Rubrene OFET with TiO_2 gate dielectric results in better performance in terms of mobility as compared to SiO_2 based rubrene OFETs due to the better surface energy matching of the two.

Keywords: Rubrene, organic field effect transistors, OTS treatment, contact angle, surface energy.

1. Introduction

The quality of OSCs and dielectric materials determine the performance of OFETs. The potential improvements in V-I characteristics of OFETs would depend on the dielectric surface properties such as surface energy and surface roughness [1]. In the growth process of OSCs on the dielectrics, the surface-induced morphology at the first few monolayers strongly influence the mobility [2]. In order to develop high performance OFETs, it is required to control the interface property of the OSCs and dielectrics precisely. In many investigations, the surface property of thermally grown SiO_2 is modified by surface treatment using different SAMs. Most of the researchers have used OTS monolayer for the dielectric surface treatment to improve the performance of OFETs [3]. The electrical characteristics of OFETs can be improved by controlling the dielectric surface energy which in turn can influence the quality, morphology and the structure of the OSCs layers. The usage of contact angle measurement in the calculation of surface energies are well established and discussed in the literature [4,5]. Klauk et al. have fabricated pentacene FETs using poly(4-vinyl phenol) copolymer and cross-linked poly(4-vinyl phenol) as polymer gate-dielectric layers and obtained mobilities as high as 3 cm²/Vs [6]. These results indicate that the control of surface energy in gate dielectrics can dominate the electrical performance of OFETs by

influencing the morphology and structure of the active layer. Yoshida et al. have reported on the effect of modifying the SiO_2/Si substrate by spin-coating several kinds of polymer thin films such as poly(vinylidenefluride), polystyrene, poly(methyl methacrylate) and poly(vinyl alcohol) which exhibited different surface energies owing to the different functional groups [7]. They reported that as the surface energy of the polymer modifier increased from 35 mJ/m^2 to 47 mJ/m^2, the grain size of the pentacene film and carrier mobility increased. But at the higher surface energy of 63 mJ/m^2, the grain size of the pentacene film and carrier mobility abruptly decreased.

In this paper, surface properties of both untreated and OTS surface treated SiO_2 and TiO_2 dielectrics were analyzed by measuring the contact angle using water and di-iodomethane. The contact angle between water and the dielectric surface is analyzed using the software program Image. The resultant surface free energy between rubrene and the insulator was also reduced. The performance of OFETs with untreated dielectric in terms of mobility was compared with other OFETs fabricated with OTS treated dielectric layer.

2. Experimental methods

A heavily doped Si-wafer (resistivity 1–10 ohm-cm) and thermally evaporated gold was used as substrate and gate electrode respectively. Thermally grown SiO_2 and e-beam evaporated TiO_2 dielectric layers, each of 200 nm thickness were fabricated. Source and drain electrodes were fabricated by means of thermal evaporation with shadow masking. OFET devices were fabricated in the top-contact geometry. Source-drain width and length are 3000µm and 30µm respectively. After that, all samples were cleaned in ultra-sonic bath using acetone and methanol for10 minutes to remove most of the surface organic contaminants. After that, they were rinsed in de-ionized water and purged using pure nitrogen gas to be wet-cleaned sample. Prior to the deposition of the rubrene as active layer, the SiO_2 and TiO_2 gate dielectrics were treated by means of OTS treatment [8]. For the OTS treatment, wet-cleaned dielectric samples were dipped in the OTS solution for 10 seconds and washed out with acetone. After these treatments, rubrene was deposited by thermal evaporation method. To analyze the surface state of the dielectrics, the oxide surfaces were characterized by measuring the contact angle with de-ionised water and di-iodomethane after OTS surface treatment. The contact angle was measured by contact angle measurement system (Holmarc Opto-Mechatronics Pvt. Ltd.) and surface free energy was calculated. De-ionised water and di-iodomethane were chosen as the testing liquids. Charge carrier mobility of Rubrene OFET was estimated from the I-V characteristics plotted using semiconductor parameter analyzer (B1500A, Agilent).

3. Results and Discussion
3.1. Surface free energy of SiO_2 and TiO_2

In the present work, Owens and Wendt and Kaelbel (OWK) models have been used to determine the surface energy of SiO2 and TiO2. According to the OWK model [9], the surface energy (γ_s) is the sum of polar (γ_s^p) and dispersive (γ_s^d) components and is given by the equation:

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{1}$$

The two terms γ_s^p and γ_s^d are computed by solving the equation:

$$\gamma_{lv}\left(1+\cos\theta\right) = 2\left(\gamma_s^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_s^p \gamma_{lv}^p\right)^{1/2} \tag{2}$$

Because of the presence of two unknowns (solid surface free energy and solid-liquid interfacial free energy) in OWRK technique, two liquids with known dispersive and polar components of surface energy are required to estimate the solid surface free energy. The two liquids used are water and di-iodomethane (CH_2I_2) and the data of surface energy are shown in Table 1.

Table 1: Surface energy parameters of Liquids used for estimation [10,11].

Parameters	Surface energy parameters (mJ/m^2)	
	Water	Di-iodomethane (CH_2I_2)
γ_{lv}	72.8	50.8
γ_{lv}^{p}	46.4	0.0
γ_{lv}^{d}	26.4	50.8

The contact angle (θ) of equation 2 is measured experimentally and the average values are computed for the different gate dielectrics using the two fluids and the results are shown in Table 2. The measured contact angles of surface treated SiO_2 and TiO_2 layers are shown in Table 2 and 3.

Table 2: Contact angle of untreated gate dielectrics.

Samples	Contact angle (°)	
	Water	Di-iodomethane (CH_2I_2)
SiO_2	43	16.3
TiO_2	78.5	36.2

Table 3: Contact angle of surface treated gate dielectrics.

Samples	Contact angle (°)	
	Water	Di-iodomethane (CH_2I_2)
SiO_2-OTS	68	27
TiO_2-OTS	85	45

The estimated surface energy of the different gate dielectrics on the basis of this model by measurement of the contact angle is tabulated in Table 4. The polar component of surface energy defines the hydrophilic surface property, whereas the dispersive component defines the hydrophobic property. It is observed that the different gate dielectrics possess different surface energy. The surface energy values of the surface treated SiO_2 and TiO_2 dielectric are shown in Table 5.

Table 4: Surface energy of gate dielectrics.

Samples	Surface energy (mJ/m^2)		
	γ_s^d	γ_s^p	γ_s
SiO_2	48.86	15.84	64.7
TiO_2	40.96	2.22	43.18

Table 5: Surface energy of surface treated gate dielectrics.

Samples	Surface energy (mJ/m^2)		
	γ_s^d	γ_s^p	γ_s
SiO_2-OTS	45.43	5.11	50.54
TiO_2-OTS	36.97	1.49	38.46

It is observed that the surface energy decreases with the surface modification and further the polar component is observed to be more effectively reduced after OTS surface treatment. This is mainly due to changes in surface molecular structure which results in variations in the magnitude of contact angle with water. The hydrophilic property of a dielectric is observed to be more sensitive to OTS treatment as shown by the contact angle. The higher value of contact angle and

lower value of surface energy is the characteristic of hydrophobicity of the dielectric surface as shown in Fig. 1 for the SiO$_2$/Si substrate and OTS-treated SiO$_2$/Si substrate. This is very well correlated with the results shown in Table 2, 3, 4 and 5. The surface treatment results in decrease in the polar component which in turn decreases the total surface energy of the gate dielectric. Comparatively better results are obtained in the case of OTS treated dielectric surfaces since surface energy is lower in comparison to the other SAMs.
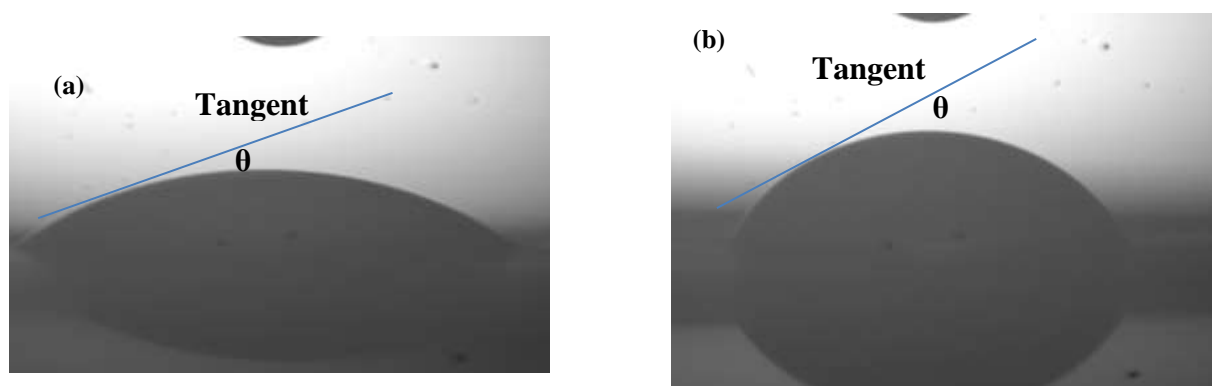
Fig. 1: Photograph of the droplet during contact angle measurement: (a) SiO$_2$/Si substrate (b) OTS-coated SiO$_2$/Si substrate.

From Fig. 1, it can be observed that the untreated SiO$_2$ surface possess a water contact angle of 43° and the corresponding surface free energy of 50.54 mJ/m^2 [12] due to the surface being hydrophilic in nature. This is because SiO$_2$ is basically an amorphous material in which each Si atom binds with four oxygen atoms in a tetrahedral geometry. The surface of the material is characterized by the presence of two different kinds of bonds such as silanols (Si-OH) and siloxanes (Si-O-Si). The higher density of silanol tends to make the surface hydrophilic in nature. The OTS-treated SiO$_2$ surface possess a water contact angle of 68° and the surface free energy of 38.46 mJ/m^2 [12] which indicates that the surface is hydrophobic in nature. The increase in contact angle of water with OTS-treatment makes the SiO$_2$ surface more hydrophobic in nature and hence decreases the surface energy. This suggests that the OTS attached with chains of long alkyl, alters the surface property.

3.2. Surface free energy of rubrene
The surface energy difference between OSC and the gate dielectric determines the growth mode of the thin film. This may be due to the change in dielectric surface energy which results due to change in the grain size of OSC. Therefore, contact angle of rubrene OSC is measured and shown in Fig.2. Their corresponding surface energies are computed and are shown in Table 6 and Table 7.
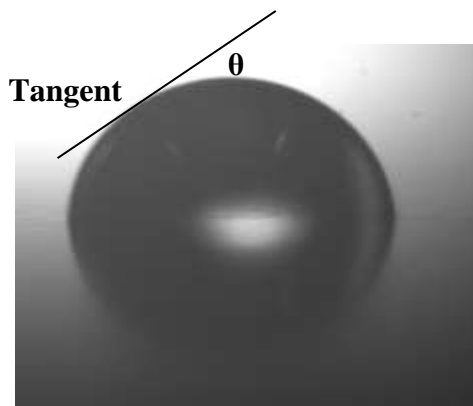

Fig. 2: Photograph of the droplet during contact angle measurement of rubrene.

Table 6: Contact angle of rubrene.

Sample	Contact angle (°)	
	Water	Diiodomethane (CH₂I₂)
Rubrene	76.4	38.5

Table 7: Surface energy of rubrene.

Samples	Surface energy (mJ/m²)		
	γ_s^d	γ_s^p	γ_s
Rubrene	40.32	3.28	43.6

3.3. Electrical characteristics of Rubrene OFETs
3.3.1. I-V characteristics of Rubrene OFETs with SiO₂ as gat

The output characteristics (I_{DS} vs. V_{DS}) at a gate-source voltage (V_{GS}) of -50 V and the drain-source voltage (V_{DS}) of 0 to -50 V of SiO₂ and OTS-treated SiO₂ were determined and the results are shown in Fig. 3a-b. It is observed that the devices exhibit typical p-type OFET characteristics. The field effect mobility (μ) of the OFET is estimated from the slope of the plot of square root of I_{DS} vs V_{GS} and by using the following equation in the saturation region
.

$$I_{DS,sat} = \left(\frac{WC_i}{2L}\right) \mu_{sat} (V_{GS} - V_T)^2 \tag{3}$$

It is observed that SiO₂ when treated with OTS prior to deposition of rubrene yields highest drain current (I_{DS}) of 390 µA at the lower gate bias of -20 V. Further, the device exhibits higher field effect mobility of 1.36 cm²/Vs and on/off current ratio of 10^7 under ambient conditions. It is noteworthy to mention that the field effect mobility achieved is much higher than those of rubrene crystalline films grown on bare SiO₂. This indicates that the surface modification of SiO₂ increases the accumulation of charges at the OSC/insulator interface by reducing the trap states substantially and this in turn improves the performance of the device due to better surface energy matching between rubrene and OTS-treated SiO₂ gate dielectric surface [13].
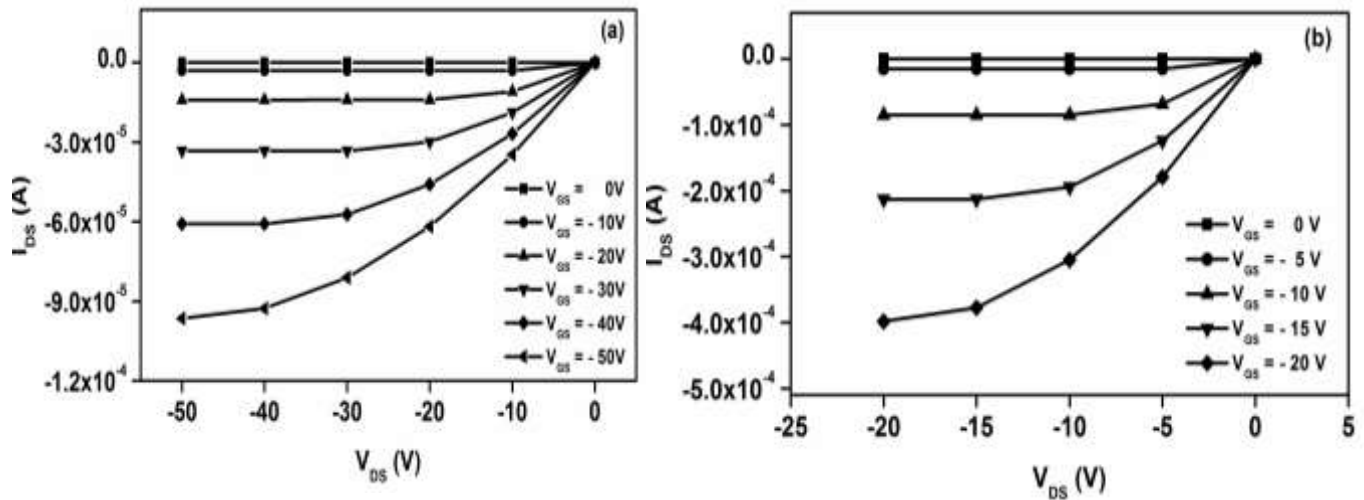

Fig. 3: Electrical characteristics of Rubrene OFETs with (a) SiO₂ gate dielectric (b) OTS-treated SiO₂ gate dielectric.

3.3.2. I-V characteristics of Rubrene OFETs with TiO₂ as gate dielectrics

Fig. 4a-b shows the variation of I_{DS} with V_{DS} and V_{GS} of rubrene based OFETs with and without modification layers of TiO₂. The OTS treated and untreated OFET devices have shown p-type OFET characteristics. The mobility of the devices based on the experimentation for I_{DS} in the saturation regime has been computed. The OFET device with TiO₂ gate dielectric alone exhibit a lower mobility of 0.196 cm²/Vs. After modification, the mobility improves to 1.98 cm²/Vs (OTS-modified). Higher mobility is certainly because of the fact that rubrene channels by then have been mostly covered

by the crystalline phase. This shows that, in the OTS modified OFET devices; there are much fewer shallow trap states and better surface energy matching, which are influencing the mobility [14].
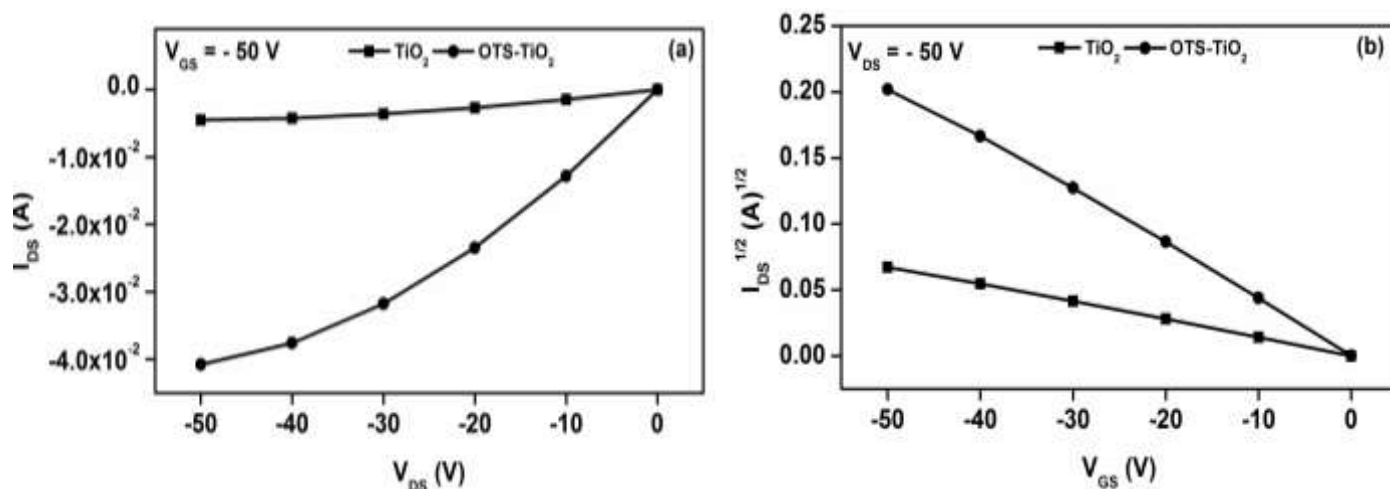

Fig. 4: V-I characteristics of OFET for TiO_2 and OTS-TiO_2 (a) Output characteristics (b) Transfer Characteristics.

4. Conclusion

1. The surface energy of SiO_2 and TiO_2 have significant impact on the performance of Rubrene OFET in terms of mobility.
2. Charge carrier mobility is observed to be increased from 0.049 to 1.36 cm^2/Vs when the SiO_2 dielectric surface energy was decreased from 64.7 mJ/cm^2 to 50.54 mJ/m^2 after OTS-treatment.
3. The surface energy matching between dielectric and OSCs enhances the OFET charge carrier mobility which in turn decreases the threshold voltage
4. Rubrene OFET with TiO_2 gate dielectric results in better performance as compared to Rubrene OFET with SiO_2 due to the better surface energy matching of the two.

Acknowledgements

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