3-((2′:2″,5″:2‴-TERTHIOPHENE)-3″-YL) ACRYLIC ACID AS ORGANIC FIELD EFFECT TRANSISTOR FOR DNA SENSING

K. C. Aw[1], N. Tjitra Salim[2], H. Peng[3], J. Travas-Sedjic[3] and W. Gao[2]
[1] *Mechanical Engineering*
[2] *Chemical and Materials Engineering*
[3] *Chemistry*
The University of Auckland, New Zealand

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Abstract: The aim of this paper is to demonstrate the use of organic field effect transistor (OFET) as a DNA sensor. We have synthesized a functionalised terthiophene monomer 3-((2′:2″,5″:2‴-terthiophene)-3″-yl) acrylic acid (TAA) and has been successfully electrodeposited as an active layer of an OFET. The polymer was oxidised in order to increase its conductivity. A mobility of 0.25 cm^2/V.s was achieved with an oxidising potential of 0.9 V. A preliminary DNA sensing test was performed on the OFET with poly TAA as active layer and a shift in threshold voltage was observed after DNA immobilization and hybridization, showing its potential as DNA sensor.

1 INTRODUCTION

Previous studies (Peng, Zhang, Spires et al l, 2007; Zhang, Peng, Kilmartin et al, 2007) have shown the ability of the acid-functionalised conducting polymers to detect DNA hybridization, where carboxylic acidic functionality enabled covalent attachment of biomolecules such as DNA (oligonucleotides).

However, in this research the DNA detection will be based on an organic field effect transistor (OFET) device instead of the change in impedance of an organic thin film as in Refs 1 and 2. The OFET device as a sensor can be more sensitive due to the ability to control OFET conduction via a third terminal called "gate".

2 EXPERIMENT PROCEDURES

The synthesis of 3-((2′:2″,5″:2‴-terthiophene)-3″-yl) acrylic acid (TAA) monomer is based on work by (Peng et al, 2007). The monomers were electropolymerized on a prefabricated substrate consisting of a source (S), a drain (D) and a gate (G) terminals. The bottom gate was a highly doped Si and a 100 nm SiO_2 acted as the gate dielectric. Finally, the two gold contacts as S and D with an effective channel width of 5560 μm were patterned on top of the SiO_2. Channel length spacing of 25, was used. The schematic structure of the OFET is illustrated in Figure 1.

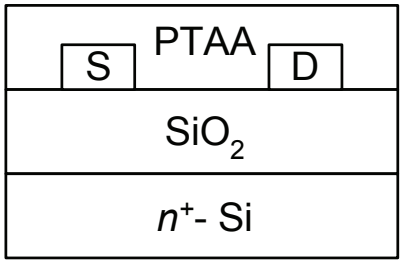

Figure 1: The schematic structure of bottom contact, bottom gate PTAA-based OFET.

The electropolymerisation was performed using the cyclic voltammetry from 0 to 1.3 V at scan rate of 50 mV/s by a CH Instrument electrochemical workstation (Model 440, CH Instruments, USA). The gold S and D contacts on the substrate were used as the working electrodes during electropolymerisation. A Pt wire and Ag/AgCl (3 M KCl) were used as the counter electrode and the reference electrode, respectively. The polymerisation solution comprised of 0.05 M tetrabutylammonium trifluoromethanesulfonate and 0.005 M TAA in acetonitrile. The obtained polymer

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TAA (PTAA) film was then oxidised in a monomer free solution by a constant potential method for 5 minutes to achieve different doping levels, therefore different conductivities. Five oxidising potential (V_{OX}) of 0.1, 0.2, 0.6, 0.9 and 1.1 V were chosen to investigate their effect on the performance of the fabricated OFET. The arrangement for electropolymerization is shown in Figure 2.

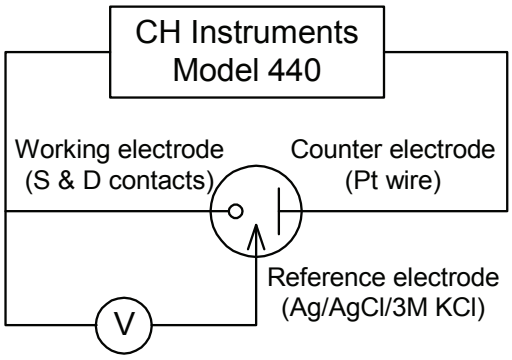

Figure 2: The electrodes arrangement for electro polymerization.

The OFET electrical characteristic was measured using Keithley 2602 source measure unit after the doping process. The microstructure of PTAA film on the Si substrate was examined using the scanning electron microscope (SEM).

Following the optimisation of PTAA-OFET fabrication process, DNA sensing ability of this OFET was tested. The study starts with DNA immobilization, a process where single stranded DNA (ssDNA) molecules with known sequence (NH_2-GAT GAG TAT TGA TGC CGA-3) synthesized by Invitrogen Life Technologies are covalently attached to the PTAA film. To attach the ssDNA, a 40 µL of phosphate buffer (pH 5.2) containing 20 nmol ssDNA probe and 400 nmol 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) was applied on the surface of PTAA-OFET and was kept at 28 °C for 1 h. Finally, the OFET was thoroughly washed using phosphate buffered saline (PBS) solution (pH 7.4) to remove any unattached ssDNA. After immobilization, the I-V characteristics of PTAA-OFET were measured using Keithley 2602 source measure unit.

The next step to test the sensing ability of PTAA-OFET is DNA hybridization, where the complementary ssDNA is applied to the surface of OFET and hybridizes with the immobilized ssDNA via complementary base pairing to form a double helix DNA. The hybridization was carried out by incubating the PTAA-OFET with immobilized DNA in PBS solution containing complementary ssDNA samples for 1 h at 42 °C. After hybridization, the OFET was washed three times using PBS solution to remove any non-hybridised ssDNA. Then I-V characterisations were carried out to determine the effect of hybridization on the OFET performance.

3 RESULTS AND DISCUSSIONS

The PTAA-OFET was electrically characterized for diferenct V_{OX} and highest calculated carrier mobility of 0.25 cm^2/V.s at $V_{D,sat}$ = -20 V is achieved with V_{OX} = 0.9 V and threshold voltage (V_T) of approximately 7 V (Tjitra Salim, Aw, Peng, et. al., 2008). Figure 3 show the OFET characteristics of PTAA oxidised at 0.9 V where the highest carrier mobility was achieved. The I-V characteristic is not of good quality due to the fact that electropolymerization process could produce film with high structural and conjugation defects (Roncali, 1992)

The above-mentioned results are in good accordance with the cyclic voltammogram (CV) of PTAA obtained in a monomer free solution as shown in Figure 4. From this CV, two anodic peaks at +0.6 V (A) and +1.05 V (B) are observed. The first anodic peak marks the beginning of polymer oxidation, indicating the formation of polaron and subsequent bipolaron formation, i.e. the charge carrier (holes) (Chen and Inganas, 1996). Therefore, one can see that the PTAA film is in a neutral state with low charge carriers (holes) density when V_{OX} < 0.6 V. With increasing V_{OX}, the PTAA starts to be oxidised, increasing the charge carrier density, which in turn would increase its conductivity. A higher conductivity PTAA film as an active layer is considered to be responsible for the increase in μ of an OFET. When $V_{OX} \geq$ +1.05 V (at the second anodic peak), a strong increase in the anodic current is observed, indicating the beginning of polymer oxidative degradation. This explains the low transistor performance when PTAA as an active layer was oxidised at voltage greater than 1 V.

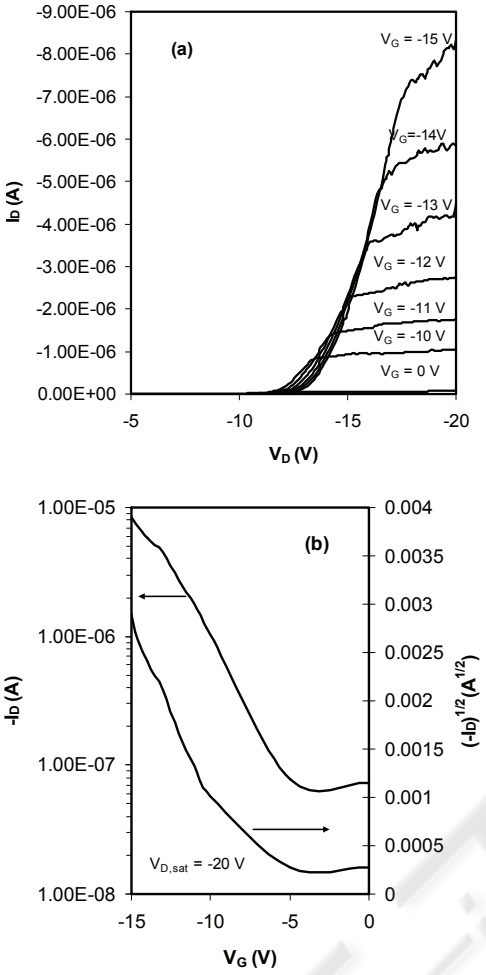

Figure 3: The I-V characteristics of bottom contact, bottom gate PTAA-based OFET with VOX = 0.9 V; (a). Output curves (ID-VD) at different gate voltages; and (b). Transfer curves (ID-VG) in saturated regime at constant source-drain voltage of -20 V (left scale) and square root of the absolute value of ID as a function of VG (right scale).

The morphology of PTAA film on top of gold (S and D) contacts and across the channel is shown in Figure 5, demonstrating that the electrodeposition of PAA enables the creation of active region between the S and D contacts creating an OFET.

A preliminary DNA sensing ability of PTAA-OFET was tested and the results are shown in Figure 6. A shift in threshold voltage (VT) was observed after DNA immobilization and hybridization of complementary DNA, confirming the sensing ability of PTAA-OFET. Initially, the PTAA-OFET obtained a threshold voltage (VT,i) of -8 V and after DNA immobilization, the threshold voltage has shifted to about -6 V (VT,im). This positive VT shift is expected as the phosphate groups on the DNA

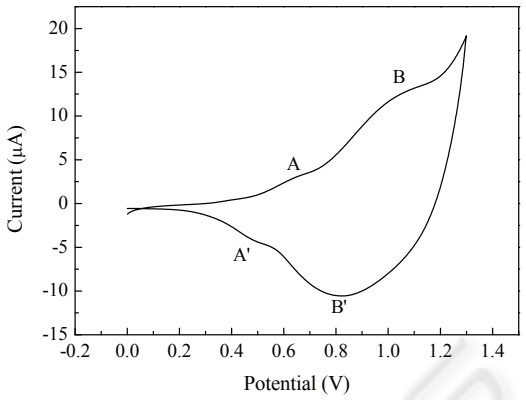

Figure 4: The cyclic voltammogram (CV) of PTAA film in a monomer free solution with a scan rate of 50 mV/s.

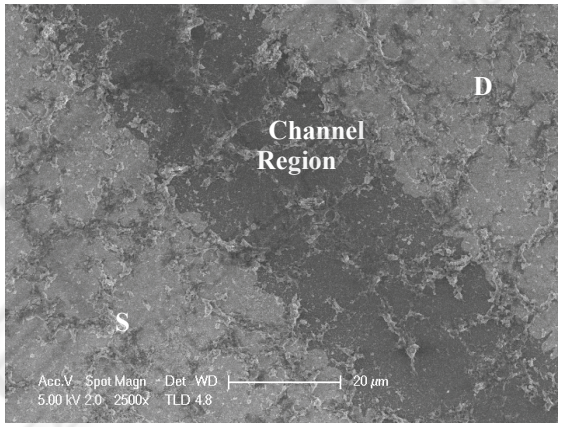

Figure 5: SEM images showing the morphology of PTAA film on top of the gold (S and D) contacts and across the channel.

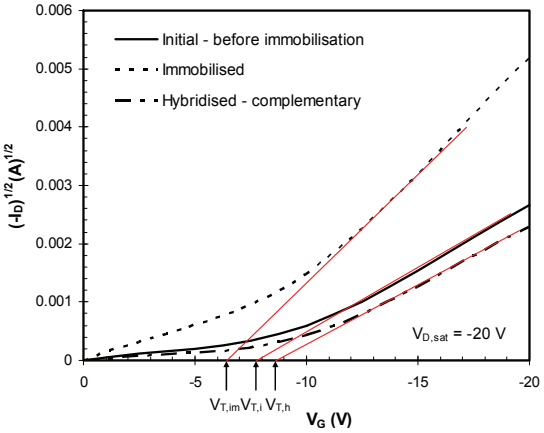

Figure 6: The √ID vs VG at VD,sat = -20 V showing the threshold voltages (VT) of bare PTAA-OFET, immobilized PTAA-OFET and hybridized PTAA-OFET with complementary DNA.

backbone are able to attract electrons from the organic semiconductor, increasing the hole concentration of PTAA than before DNA immobilization (Zhang and Subramanian, 2007). The increased in holes concentration would result in the shift of V_T to a lower negative voltage (positive shift), causing an effective *p*-doping of PTAA.

After the hybridization with complementary DNA, the threshold voltage (V_T) shifted more negatively (negative shift) to approximately -9 V. Hybridization with complementary DNA would result in double stranded DNA (dsDNA), where the bases of two complementary single stranded DNA (ssDNA) would pair up and form the double helix. According to (Zhang and Subramanian, 2007), dsDNA molecules could not be immobilized (attached) to the organic semiconductor (PTAA) as effectively as ssDNA molecules. This would result in less interaction between DNA backbone and PTAA that are known to be able to attract electrons, lowering the holes concentration in PTAA and hence, increasing the OFET's V_T to be more negative. The low interaction ability between dsDNA and PTAA is because the bases of DNA are not exposed in dsDNA. The bases of DNA are responsible to the hybrophobic interaction, resulting in physical adsorption between ssDNA and PTAA, i.e. immobilization of ssDNA.

4 CONCLUSIONS

The PTAA based p-channel OFETs were fabricated successfully with a μmax of 0.25 cm^2/Vs. The amount of doping through the V_{OX} in PTAA is crucial in controlling the μ of the OFET. An optimum V_{OX} of 0.9 V was obtained, producing OFET with the highest μ. A V_{OX} > 1.0 V causes degradation to the PTAA film, leading to poor charge mobility, while $V_{OX} \leq 0.2$ V does not produce sufficient doping. These results demonstrated that the μ of FET fabricated with PTAA can be controlled by V_{OX} and correlates with the potential value of the cyclic voltammogram for 0.2 V ≤ V_{OX} < 1.1 V. A preliminary DNA sensing test was performed on the PTAA-OFET and a shift in threshold voltage was observed after DNA immobilisation and hybridisation, showing its potential as DNA sensor. However, more detailed study is required to realise this PTAA-OFET as DNA sensor before it can be deployed.

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