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Fabrication of p-type Organic Field Effect Transistor using PMMA:TiO_2 as Nanocomposite Dielectric Layer

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Abstract. This paper report on the fabrication of p-type organic field effects transistor (OFET) using low temperature spin coating deposition technique. The p-type OFETs were fabricated using poly (3-hexylthiophene-2,5-diyl) (P3HT) and poly (methyl methacrylate):titanium dioxide (PMMA:TiO_2) nanocomposite material were used as semiconductor and the gate dielectric, respectively. The electrical and structural properties of OFETs were analysed using current-voltage (I-V), atomic force microscopy (AFM) and RAMAN spectroscopy. Results from I-V show that the fabricated p-type OFET has moderate performance with threshold voltage, V_{TH} is -3V and mobility, μ is 2.01 $cm^2\ V^{-1}s$.

1. Introduction

Organic field effect transistor (OFET) is an example of organic electronics devices and has attracted a great deal of attention to be utilized in integrated circuit (IC) [1]. OFET structure consists of semiconductors, dielectric layer and electrodes that fabricate using organic or polymer material. OFETs is suitable to be used for low voltage application such as smart labels, driving matrices for organic flat panel displays [2], sensor [3] and food industry [4]. The innovation of OFET has grown in recent years and have been focused on the development of improving the properties of organic semiconductor materials and methods for improving the material to achieve high carrier mobility [5, 9-11]. Carries mobilities is an important parameter in determining and enhancing the OFET performance because OFET basically operates through the modulation of charge carrier flow at the interface of semiconductor-dielectric.

In order to investigate the OFET performance, metal-insulator-semiconductor (MIS) structure was used to investigate the behaviour between the insulator and semiconductor. The performance of MIS capacitor is strongly depend on semiconductor and dielectric layer. The important characteristics for MIS is the accumulation/depletion behaviour, charge transport and trapping, interface effects between insulator and semiconductor [1]. In order to obtain good MIS characteristics, the interface between insulator and the semiconductor layer must be well-matched because the insulator were sandwiched between the semiconductor and ohmic metal contacts and the bias voltage is being applied across an insulator. The same characteristics and principles was applied to the MIS that fabricated using organic material in the case poly (3-alkylthiophene) (P3HT) and poly (methyl methacrylate): titanium dioxide (PMMA:TiO_2).

(P3HT) [18] is a stable p-type organic semiconductor material and the most prominent organic semiconductor material that has been widely being used by other researcher in fabricating the organic electronic devices. Polythiophenes, in particular (P3HT), are the most prominent and investigated representatives of semiconducting polymers and have been applied in various devices such as solar cells and field-effect transistors. For this class of polymers, it has been well established that the morphology of the functional layer has a significant impact on the device performance. For insulator layer, the nanocomposite material between PMMA and TiO_2 was used due to its high dielectric permittivity, ε' that has been optimized from our previous work. Besides having high dielectric permittivity, (ε' ~ 12), PMMA:TiO_2 also have high capacitance for storage purpose and it can be processor at low temperature [12].

In this paper, we report the fabrication and characterization of metal-insulator-semiconductor (MIS) and p-type organic field effect transistor (p-OFET) using PMMA:TiO_2 nanocomposite and P3HT as insulator and semiconductor layer, respectively. Both thin film was deposited by spin coating onto glass substrate and characterized by current-voltage (I-V), atomic force microscopy (AFM) and RAMAN spectroscopy. In this work, we only concentrate on the I-V characteristics of MIS and p-type OFET.

2. Experimental Setup

Before coating, the glass substrate was clean by sonication method in acetone, methanol and de-ionized (DI) water in ultrasonic bath for 10 min at 50 °C, then dried using nitrogen (N_2) gas.

2.1. Fabrication of PMMA:TiO_2 Nanocomposite dielectric film

PMMA:TiO_2 solution was prepared by dissolving 0.3g of PMMA (Sigma Aldrich) and 3wt% of TiO_2 nanopowder in 5ml of Toluene. A few drops of TMOMS were added into PMMA: TiO_2 as stabilizer between PMMA and TiO_2 nanopowder. Then, the solution was sonicated for 30 min at 50 °C before being stirred for 24 hrs. The deposition of PMMA: TiO_2 thin film was done in a spin coater with argon (Ar) gas at 4 mbar, 0.5 s/lit. The time and spin speed of spin coater were fixed to 4000 rpm for 60 sec in order to obtain the uniform PMMA: TiO_2 nanocomposite film. 2 drops of PMMA: TiO_2 solution was dropped onto the substrate and the rotation would evenly spread the solution, and stop automatically after 60 sec. The substrate with a layer of 2 drops was then dried at 50 °C for 5 minutes to evaporate the solvent and harden the coating. After that, the PMMA: TiO_2 films were annealed at 120 °C for 30 minutes, enough to sufficiently remove the remaining solvent.

2.2. Fabrication of P3HT Thin Film

P3HT solution was prepared by dissolving 15mg of P3HT powder (Sigma Aldrich) in 15 ml of chloroform solvent (Eriendemann Schmidt). The solution was sonicated for 30 min at 50 °C before being stirred for 24 hrs. The P3HT film was deposited using spin coating technique. The spin speed was fixed at 1500 rpm for 60 sec. Then, the P3HT film is dried at 50 °C for 5 min to evaporate the solvent.

2.3. Fabrication of P3HT Thin Film

The MIS (Al/P3HT/PMMA:TiO_2/Al) structure as shown in Fig. 1 were fabricated to investigate the performance of OFETs. The MIS device were fabricate on top of glass substrate. 60 nm thick of aluminum (Al) were evaporate on top of glass substrate to form bottom electrode. P3HT solution were spin coated on top of Al electrode using the same technique to form P3HT thin film. Then, PMMA:TiO_2 nanocomposite dielectric film were deposited on top of P3HT thin film followed by deposition of 100 nm thick Al to form top electrode.

The fabrication of p-type OFET start by depositing the P3HT semiconductor layer on glass substrate. Al source and drain terminals were deposited using thermal evaporator technique. Then, a 500 nm thick of PMMA:TiO_2 nanocomposite dielectric were deposited on top of source and drain terminal act as dielectric layer. Then, Al gate electrode with 100 nm thick were deposited on top of PMMA:TiO_2 layer. Complete p-type OFET structure as shown in Fig. 2 below.

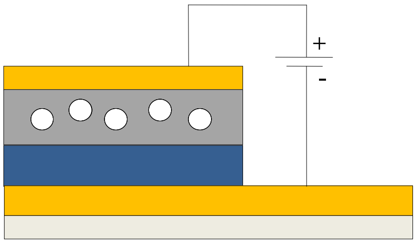

Figure 1. Schematic structure of the MIS

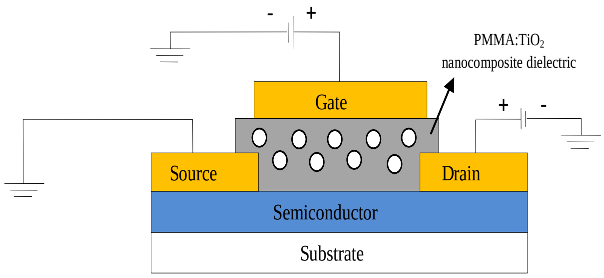

Figure 2. Schematic diagram of the OFETs

3. Results and Discussions

3.1. Structural Properties

The Raman spectrum of PMMA:TiO_2 nanocomposites and P3HT thin film are shown in Fig. 3. It can be seen that there is most of the Raman bands for PMMA:TiO_2 are identified are the same as Raman band for PMMA that has been reported in the literature [21,22]. The spectrums for PMMA:TiO_2 occur at 2957, 1460 cm^{-1} and weak features at 3001 cm^{-1} are belonging to the C-H vibration. The features at 2848 cm^{-1} is corresponding to the infrared spectrum [23]. The feature at 999 cm^{-1} was assigned to OCH3 rock, the feature at 1081 cm^{-1} to v(C-C) skeletal mode vibration. The observed bands are at 602, 1460 and 1736 cm-^{1}. A new peaks which can be seen in PMMA:TiO_2 curve are at 141 cm^{-1} indicate the presence of TiO_2 nanoparticles which associated with rutile phase [24]. The 715 cm^{-1} , 1380 cm^{-1} and 1440 cm^{-1} Raman peaks indicated by squares are assigned to the P3HT C–S– C ring deformation, C–C skeletal stretching and CLC ring stretching, respectively.

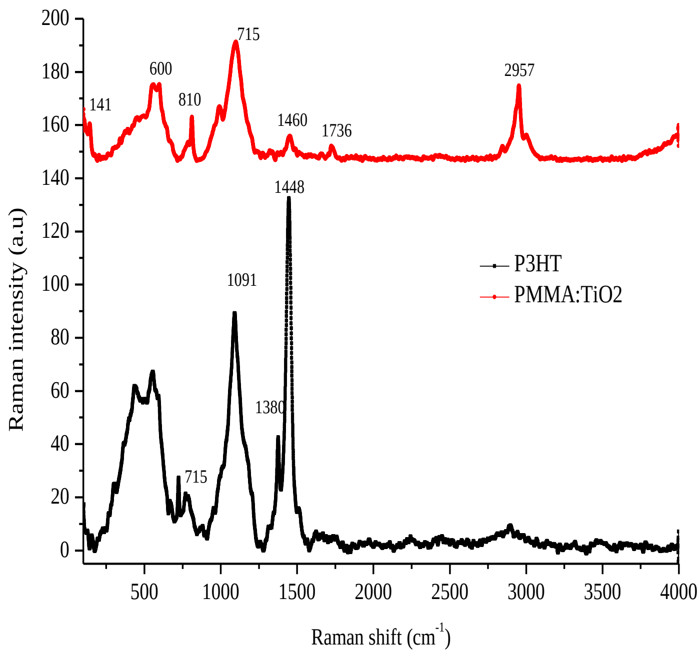

Figure 3. RAMAN spectrum of P3HT and PMMA:TiO_2 film.

Figure 4 and Fig.5 is an FESEM image displaying the surface morphology of PMMA:TiO_2 nanocomposite films and cross-section image of P3HT/PMMA:TiO_2 thin film on glass substrate. As can be observed, the surface of the nanocomposite PMMA:TiO_2 is not smooth and there is agglomerated particles at certain area. This agglomerated particle is confirmed that there is a formation of non-homogenous organic-inorganic materials with very small domain in the nanometric scales. The root mean square (rms) roughness of the film measured in this area is 72.903 nm for nanocomposite PMMA:TiO_2. The topography of P3HT films were observed by AFM as shown in Figure 6. The surface roughness in root mean square (RMS) data is 0.94 nm. This suggests that the P3HT molecules are slightly more densely packed, and hence slow down the diffusion of oxygen and moisture to the gate dielectric interface where the holes transport takes place. This may also contribute to the improved stability for the P3HT devices based on PMMA:TiO_2 coated substrates.

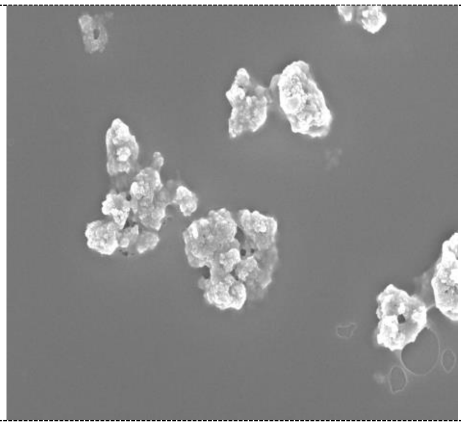

Figure 4. FESEM images of PMMA:TiO_2 thin film.

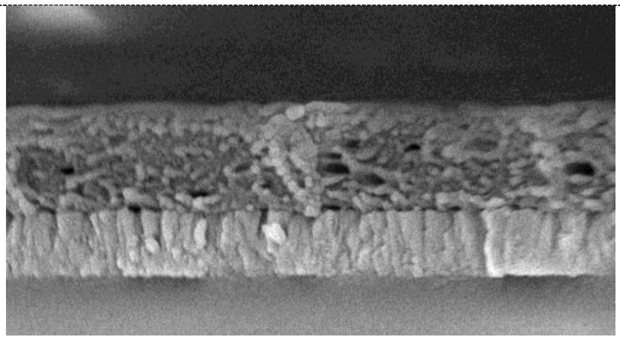

Figure 5. Cross-section image of P3HT and PMMA:TiO_2 film.

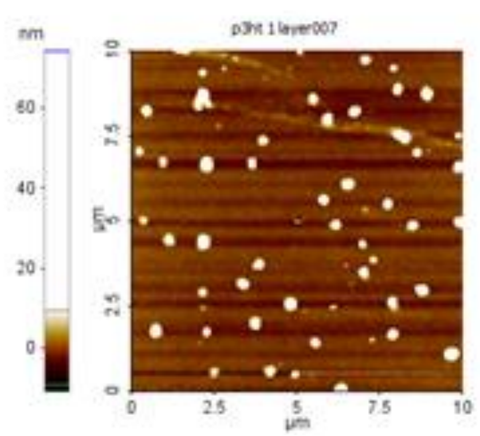

Figure 6. AFM image of P3HT thin film.

3.2. Electrical Properties of MIS and p-type OFET

The purpose of fabricating the MIS devices is to investigate the suitability and the compatibility of fabricated PMMA:TiO_2 nanocomposite dielectric layer with p-types semiconductor which is P3HT film. I-V characteristics of MIS with different annealing temperature of P3HT film are shown in Fig.7 below. The purpose of varying the annealing temperature is to obtain the optimization temperature to deposit the P3HT thin film for OFET fabrication. The applied voltages were sweep from +10 V to -10 V to the Al bottom electrode while top Al electrode was grounded. I-V curve for all MIS samples show nonlinear or rectifying behaviour with different operating voltages. The operating voltages are increased significantly when the annealing temperature of P3HT film increased. MIS device with 60 ^oC has the lowest operating voltage ~ - 7 V and MIS with 180 ^oC has the highest operating voltage which is – 1.0

V. Increment in the operating voltage, when different annealing temperature was used is because of the changes in the surface roughness and also reduction of P3HT thin film. Since the surface roughness is reduce, when the negative voltage is applied (V > -1 V) to the Al electrode, the majority carriers (hole) are accumulated near the surface of the P3HT layer. This causes the valence band edge bends downwards near the surfaces and closer to the Fermi level. When a small positive voltage (V < 0 V) is applied, the majority carriers (hole) are depleted because the valence band bends upward. The bands bend even more upward when applied large positive voltage (V < +2 V) so that the intrinsic Fermi level crosses over the Fermi level and at this point the minority carrier (electron) is larger than hole, the surface thus inverted. These excess electrons caused increased current in the positive.

The electrical properties of p-type OFET were characterize using 4200 semiconductor characterization system. Figure 8 shows the typical drain-source current, I_{DS} characteristics of p-type OFETs with PMMA:TiO_2 and P3HT as dielectric and semiconductor layer. The drain-source voltage, V_{DS} was varied from 0 ~ - 4 V in steps 0.1. For this p-type OFETs, negative V_{DS} were applied because P3HT is a p-type semiconductor/active material, therefore the majority carriers are holes. Figure 8 shows that the applied gate voltage, V_G was varied from -10 to +10 V. The I_{DS}-V_{DS} curves indicate that our fabricated p–type OFET, resembled the theoretically transistor curves, nevertheless, the curves are not ideal. This is due to the parallel resistance that exists in the device. It can be also seen that, apparently that the fabricated p-type OFET is in the depletion mode (normally-ON) state. When the no gate voltage, V_G (V_G = 0V) is applied, the fabricated p-type OFETs are in ON state. For these devices, since the majority carries is holes, therefore the holes channel is induced at the semiconductor-dielectric (which is P3HT- PMMA:TiO_2) interface by a negative bias applied to the gate. The current flows form source to drain electrodes via holes channel if the $-V_G$ is sufficiently high. At this condition, the channel acts as variable resistors and the I_{DS} are linear with $-V_{DS}$, which correspond to the linear region. As the $-V_{DS}$ increases, the space charge region under the channel and near the drain region widens and eventually reaches a pinch-off point condition in which the channel width becomes zero. Beyond this pinch-off point, in the saturation region, the I_{DS} become saturated or constant as $-V_{DS}$ continues to increase. By applying positive V_G, the p–type OFET start to change state from ON to OFF state. The fabricated p-type OFET in particular, there is no good saturation current observed. Figure 9 illustrated the I_{DS} versus V_{GS} by fixing the V_{DS} at -10 V. From these curves, the field effect mobility, μ_{FE} and the threshold voltage, V_{TH} were determined. The μ_{FE} was extracted from the slope of the linear plots of the square root of the I_{DS} versus the V_G. The V_{TH} was estimated corresponds to the intersection dashed lines with V_{GS} axis is -1V. Meanwhile, the μ_{FE} of the p-type OFETs is 8 x 10^{-3} cm2 /Vs^{-1}.

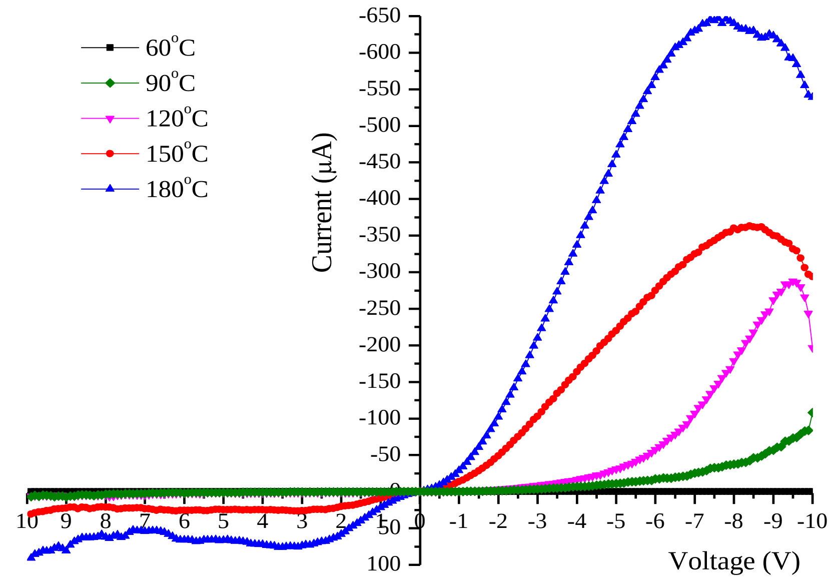

Figure 7. I-V characteristics of MIS fabricated using P3HT as semiconductor layer.

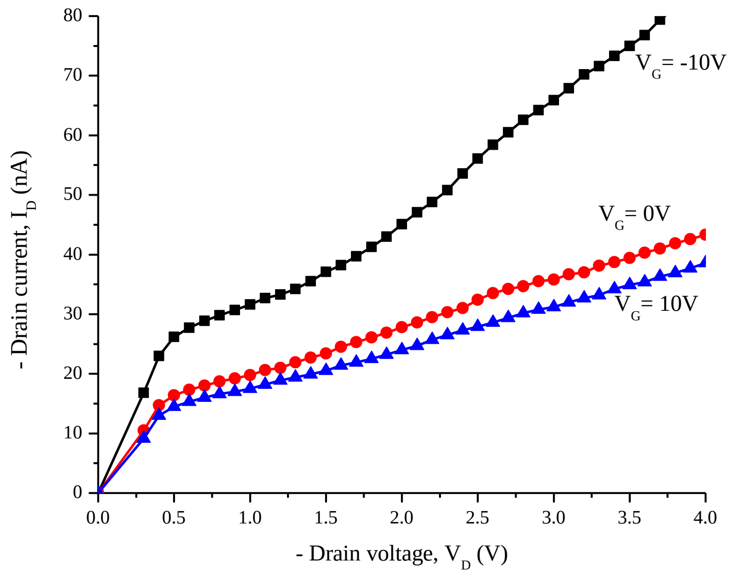

Figure 8. I_d-V_d curve characteristics curve of p-type OFET with PMMA:TiO_2 nanocomposite and P3HT as dielectric and semiconductor layer.

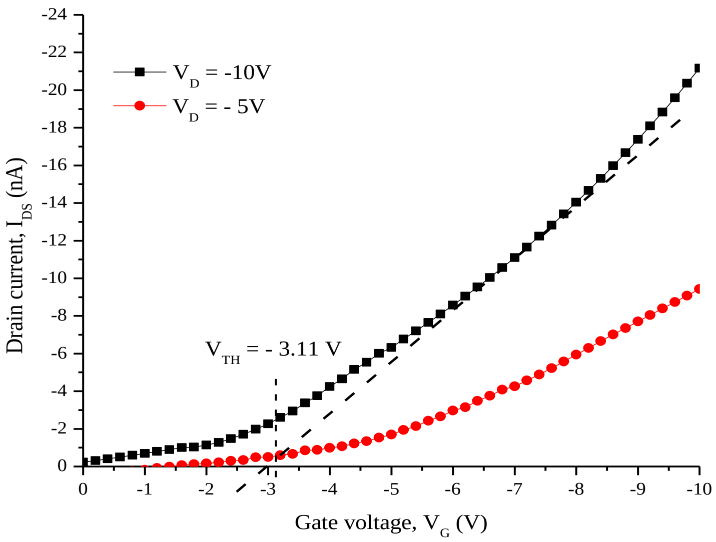

Figure 9. I_d-V_g curve characteristics curve of p-type OFET with PMMA:TiO_2 nanocomposite and P3HT as dielectric and semiconductor layer.

4. Conclusion

The fabricated MIS capacitor with different P3HT thickness and nanocomposite PMMA:TiO_2 as semiconductor and insulator, respectively on glass substrate. The results indicate that the operating voltage, V_{TH} of organic-MIS improve significantly improve when the P3HT thickness is reduce. Low surface roughness was obtained when the thickness of the P3HT film is reduce. Through its electrical properties, it was found that the insulating property of nanocomposite PMMA:TiO_2 are comparable to those usually obtained for MIS structures with other material that being use as insulator. PMMA:TiO_2 organic-inorganic films offer attractive opportunities due to its good electrical properties and an effective way to reduce the operating voltage of organic-MIS but also a useful way to investigate the interfacial capacitance that exists at the interface of semiconductor/insulator. The OFETs was subsequently fabricated and examined to identify the characteristic of organic transistor using PMMA:TiO_2 nanocomposite as dielectric layer. The fabricated p-type OFET showed a poor performance even though the real permittivity, ε' for PMMA:TiO_2 was ~ 12, about 3 times higher than the ε' for SiO_2.

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