Study on the effect of PVDF-TrFE layer to the electrical properties of MIS devices

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Abstract. This paper investigates the effect of PVDF-TrFE layer to the electrical properties of MIS device. The MIS (Al/PMMA:TiO₂/PVDF-TrFE/Si) structures were fabricated on n-type Si substrate. The results indicate that the properties of MIS improved drastically with PVDF-TrFE layer. I-V and C-V characteristics shows that the MIS has a fast operating voltage approximately 1 V, low leakage current, large capacitance. No hysteresis was observed compared to MIS without PVDF-TrFE layer. The improvement in the electrical properties of MIS (Al/PMMA:TiO₂/PVDF-TrFE /Si) is due to the increment in the real permittivity, ε’ value of the insulator.

1. Introduction
Polymer material has been applied in various electronic applications such, light emitting diode (LED) and solar cells [1]. The properties of polymer material such as light weight, high flexibility and also can be process at low temperature has be advantage if compare to inorganic material [2]. There are many polymer material have been studied to be used as insulator or dielectric layer in organic thin film transistor (OTFT) and organic field effect transistor (OFET) because some polymer material has good insulating properties which is similar and comparable with silicon dioxide (SiO₂) [3]. Poly (methyl methacrylate) (PMMA) is an example of polymer material that has been used as dielectric or insulating layer in OFET and OTFT. It has high resistivity, (10¹⁵ Ωcm) along with thermal and mechanical stability [4]. Nevertheless, using PMMA as dielectric layer in OTFT leads to high operating voltage because it has low dielectric permittivity, εᵣ (~2.6 at 1MHz) [5] and formation of pinholes at minimal film thickness [6-8]. This high operating voltage will degrade the performance of the OFET and OTFT. In order to overcome the PMMA problem, some researcher introduces compositing the PMMA with inorganic material [5-7]. There are several inorganic material such as titanium dioxide (TiO₂), zinc oxide (ZnO) and silicon dioxide (SiO₂) are an example of inorganic

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Material that being used as filler in the nanocomposite material. TiO$_2$ were selected due to several characteristics such as it has high $\varepsilon_r$ (in the range of 40 to 86 [9]. Our previous work in 2012 proven that the $\varepsilon_r$ of PMMA increased from 2.6 to 12 measure at 1 MHz [10-12]. Even though, there is remarkable improvement in the value of $\varepsilon_r$, in the point of the morphology view, the poly (methyl methacrylate): titanium dioxide (PMMA:TiO$_2$) nanocomposite film are poor. To overcome the morphology problem, buffer layer were added on top of the PMMA:TiO$_2$ film. Poly (vinylidenefluoride-co-trifluoroethylene) (PVDF-TrFE) film was selected because it has a smooth, uniform morphology and also high $\varepsilon_r$ (in range 12 ~ 40) measured at 1 MHz. Further, it has been reported that PVDF-TrFE is a semi-crystalline copolymer is miscible with other polymer for various compositions and that this binary blend could stabilize the phase morphology and improve the interfacial adhesion [13].

Metal-insulator-semiconductor (MIS) was fabricated to investigate the effect of PVDF-TrFE layer on top of PMMA:TiO$_2$ layer. MIS is a device that is formed from a layer of metal, a layer of insulating material and a layer of semiconductor material. There are several characteristics of MIS such as the capacitance value and leakage current value influence the performance of MIS devices [14]. This paper is to investigate the electrical characteristics of metal insulator semiconductor (MIS) using multilayer dielectric film. There are two samples of MIS devices with multilayer dielectric were fabricate to investigate and analyze the performance of MIS in the point of the electrical properties. MIS device with single layer dielectric film were also fabricate for comparison purpose. All MIS devices were fabricated on n-type silicon (n-Si) acting as semiconductor layer.

2. Experimental Setup

The MIS devices was fabricated on n-type Si substrate. The n-Si was used as substrate and also as semiconductor layer. The n-Si substrate was cleaned in an ultrasonic bath with acetone, methanol, de-ionized water (DI) successively for 10 minutes and then dried by nitrogen (N$_2$) gas.

2.1 MIS Device Fabrication

There are two types of MIS devices were fabricated. The first types is known as sample A consist only PMMA:TiO$_2$ layer while the second MIS (sample B) consist of PVDF-TrFE layer on top of the PMMA:TiO$_2$ layer. The single layer was fabricated for comparison purpose meanwhile the multilayer (PVDF-TrFE/PMMA:TiO$_2$) is to investigate the performance of MIS. All MIS devices were fabricated on n-type silicon (n-Si) substrates. The n-Si was used as substrate and also as semiconductor layer. The n-Si substrate was cleaned in an ultrasonic bath with acetone, methanol, de-ionized water (DI) successively for 10 minutes and then dried by nitrogen (N$_2$) gas.

2.2 MIS with PMMA:TiO$_2$ dielectric film

After the drying process of n-Si, the nanocomposite PMMA: TiO$_2$ dielectric films were prepared at 3wt% by dissolving PMMA powder and self prepared TiO$_2$ nanowire in Toluene (Sigma Aldrich). Six drops of trimethoxymethylsilane (TMOMS) was added into the solution to stabilize the PMMA and TiO$_2$. The solution was sonicated for 30 minutes at 50$^\circ$C before being stirred for 24 hours. The PMMA: TiO$_2$ were spin coated on n-Si at 4000 rpm for 60 seconds. The film is dried at 50$^\circ$C for 5 minutes to evaporate the solvent and then annealed at 120$^\circ$C for 30 minutes resulting a PMMA:TiO$_2$ dielectric film of 500 nm. Aluminum (Al) with 60 and 100 nm thick was deposited as bottom and top contact electrode using lift-off mask. The characterization of the electrical properties was performed by Keithley 4200 Semiconductor Characterization Unit for I-V and C-V measurement. All measurement was taken at room temperature. The physical thicknesses were determined using Dektak surface profiler.

2.3 MIS with PVDF-TrFE/PMMA:TiO$_2$ dielectric film

The MIS with sample B film were fabricated on n-Si substrate. The deposition methods PMMA:TiO$_2$ dielectric film is similar in subsection 2.1. The PVDF-TrFE 70/30 copolymer was
obtained from (Piezotech France). PVDF-TrFE solution was prepared by dissolving it in methyl ethyl ketone (MEK) (Sigma Aldrich) with the concentration of 15g/l. The PVDF-TrFE solution stirred for 24 hours at room temperature. Then the solution was sonicated for 1 hour at 50°C with ultrasonic water glass. The spin speed is 3500 rpm for 90 seconds. The thickness of PVDF-TrFE thin films with is approximately 70 nm. Aluminum (Al) with 30 and 60 nm thick was deposited as bottom and top contact electrode using lift-off mask. Aluminum (Al) with 60 and 100 nm thick was deposited as bottom and top contact electrode using lift-off mask. The film thickness of PMMA:TiO₂/PVDF-TrFE dielectric film were measured ~ 567 nm. The characterization of the electrical properties was performed by Keithley 4200 Semiconductor Characterization Unit for I-V and C-V measurement. All measurement was taken at room temperature. The physical thicknesses were determined using Dektak surface profiler.

3. Results and Discussion

3.1 Surface Morphology
The insulator/semiconductor interface is equally important to control because this is where the conducting channel is formed. The surface morphologies of sample A and B are shown in Figure 2 and 3, respectively. It can be seen that sample A have rough surface than sample B. TiO₂ is the cause for sample a have rough surface. However, sample A have a better performance for current to flow in the insulator to semiconductor due to the agglomeration of TiO₂. An agglomeration of TiO₂ is a volcanic rock consisting of rounded and angular fragments fused together. The agglomeration of TiO₂ can create a path from metal contact to the semiconductor layer and lead to high leakage current.

3.2 Current-voltage characteristics of MIS
I-V characteristics are important characteristics in most electronic devices. It basically to determine and understand the behavior of electronic device. In MIS device characteristics, the I-V
curves determine the threshold voltage, $V_{TH}$ in both its forward and reverse regions. Figure 4 show the $I-V$ curves of MIS device with PMMA:TiO$_2$ and PVDF-TrFE/PMMA:TiO$_2$ layer. The voltage bias was sweep from 0V to +10 V. It can be seen that $I-V$ for sample A are better than compared to sample B. The $V_{TH}$ for sample A is 1.4 V and for sample B is 4.13 V. The $V_{TH}$ values show sample A operate at low operating voltage compared to sample B. The increment in the $V_{TH}$ for sample B are due to the increment in the film thickness of the insulator layer from 500 nm to 567 nm. Different work function (eV) different between Al-PVDF-TrFE-PMMA:TiO$_2$-Si-Al might also contribute to the higher $V_{TH}$. Another characteristic to evaluate the electrical properties of MIS is to examine the leakage current densities, $J$ properties. The leakage current density is used to determine the amount of carrier tunneling through the insulator (dielectric) region in the MIS device. As addition, it also used to observe the suitability of the dielectric layer with semiconductor layer. Figure 5 show the leakage current density, $J$ characteristics for all samples. It can be seen that there is slightly difference between in the $J$ value for all samples. The $J$ value for sample A and B is $10^{-4}$ and $10^{-5}$ A/cm$^2$, respectively measured at 5 V. Other characteristics that can be obtained from $J$ curve is the ratio between current off, $I_{off}$ and current on, $I_{on}$. $I_{off}$ for all samples are in the range of $10^{-8}$ to $10^{-6}$ A/cm$^2$. It is important to keep $I_{off}$ very small in order to minimize the static power that a circuit consumes. The $I_{on}$ value is in the range of $10^{-5}$ to $10^{-4}$ A/cm$^2$.

![Figure 4. I-V curve for MIS for sample A (PMMA:TiO$_2$ layer) and sample B (PVDF-TrFE/PMMA:TiO$_2$ layer)](image)

![Figure 5. Leakage current for MIS for sample A (PMMA:TiO$_2$ layer) and sample B (PVDF-TrFE/PMMA:TiO$_2$ layer)](image)
3.3 Capacitance-voltage characteristics of MIS

C-V characteristics are other important characteristics in most MIS devices. It basically to determine the capacitance value which reflected to the amount of charger were stored in the MIS device. On top of that C-V characteristics also indicate the accumulation, depletion and inversion region occur by applying different frequency. The C-V characteristics of MIS with PMMA:TiO$_2$ and PVDF-TrFe/PMMA:TiO$_2$ dielectric were plotted as shown in Figure 6 measured 1 MHz. It can be seen that C-V curve for sample A and B shows show a typical n-type behaviour with accumulation, depletion and inversion regions. Accumulation region is define state the trap charge in the MIS device when the voltage been applied below than flat band voltage, $V_{FB}$. $V_{FB}$ indicate the separation region of accumulation and depletion. From the C-V curve, it also can be observed that both samples show the inversion strongly occur during high frequency. The capacitance for MIS at accumulation region with sample A is 24 nF while sample B just stored charge about 25 nF. Even though there is only a slight changes in the capacitance value for between MIS with sample A and B, it indicate that MIS with sample B has the capability to stored more charge compare MIS with sample A. The flatband voltage, $V_{FB}$ for both MIS can be obtained from Figure 6. There is not so much different from the $V_{FB}$ for MIS with sample A and sample B. $V_{FB}$ for MIS with sample A is -4.4 V while MIS with sample B is -2.6 V.

![Figure 6. C-V curve for MIS for sample A (PMMA:TiO$_2$ layer) and sample B (PVDF-TrFe/PMMA:TiO$_2$ layer)](image)

Table 1 show the summarization of I-V and C-V characteristics of MIS.

| MIS Device | Film Thickness (nm) | Threshold Voltage, $V_{TH}$ (V) | Leakage current, $J$ (A/cm$^2$) | Capacitance, $C$ (pF) | Flatband voltage, $V_{FB}$ (V) |
|------------|---------------------|---------------------------------|-------------------------------|-----------------------|-----------------------------|
| Sample A   | 500                 | 1.4                             | $1 \times 10^{-4}$            | 24                    | -4.4                        |
| Sample B   | 567                 | 4.13                            | $1 \times 10^{-5}$            | 25                    | -2.6                        |
4. Conclusion

In this paper, MIS device with PVDF-TrFE/PMMA:TiO$_2$ thin films were successfully fabricated. Result from the surface morphology indicate by adding PVDF-TrFE layer on top of PMMA:TiO$_2$ layer, the agglomeration problem are overcome. Result from I-V show that increment in the $V_{TH}$ value from 1.75 V using PMMA:TiO$_2$ to 5 V using PVDF-TrFE/PMMA:TiO$_2$. Nevertheless, in term of the leakage current properties there is significant improvement was observed. Result for C-V indicates that by adding PVDF-TrFE layer on top PMMA:TiO$_2$ improvement in the storage capability of MIS.

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