

## **REDUCTION OF TURN-ON VOLTAGE IN POLYMER ORGANIC LIGHT-EMITTING DIODE USING NANOPARTICLES TiO<sub>2</sub> THIN FILM AS A HOLE INJECTION LAYER**

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### **ABSTRACT**

A low turn-on voltage of polymer light-emitting diode, PLED is important for economical display application. We had fabricated the nanoparticles TiO<sub>2</sub> thin film between ITO and PDPV in Al/PDPV/ITO structure as a hole injection layer. The sol gel method synthesized of TiO<sub>2</sub> thin film was deposited using spin coating technique. It was found that TiO<sub>2</sub> has reduced the turn-on voltage of the original PLED device from 8.0 V to 5.0 V.

### **INTRODUCTION**

Polymer light-emitting diode has been increasing attention because of potential applications for flat panel displays [1-2]. One of the important tasks in developing PLED for economical application of display is to reduce the turn-on voltage, besides improving lifetime and stability. Recently, various experiments on PLEDs with inserted buffer layers and organic buffer layers also have been investigated by many researchers as the buffer layers improve the balance of holes and electrons injected to the emitter layer [3-6]. The turn-on voltage may be reduced by inserting TiO<sub>2</sub> layers between electrodes and other organic layers in the device structured. This paper reports the effect of using TiO<sub>2</sub> nanoparticles as buffer layer on the turn-on voltage of the devices. We choose TiO<sub>2</sub> buffer layer as it has a unique properties such as large band gap (3eV), transparent and absorb a small quantity of light at shorter wavelength [7] that will not effect the electroluminescence of our device. It was found that TiO<sub>2</sub> has reduced the turn-on voltage of the original PLED device from 8.0 V to 5.0 V.

### **EXPERIMENTAL DETAILS**

In this work we fabricated PLED with configuration of ITO/PDPV /Al (Fig. 1), where ITO is Indium Tin Oxide coated on the glass substrate as an anode, PDPV is poly (4,4'-difenilena difenilvinilena) as a emitting layer, TiO<sub>2</sub> as titanium dioxide as a hole injection layer and Al is aluminium thin film as cathode.

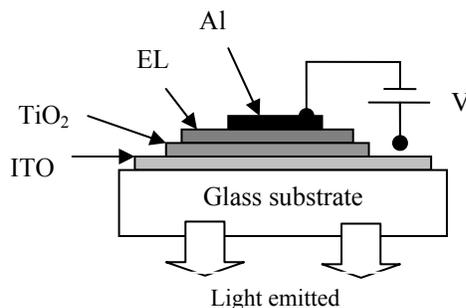


Figure 1: Structure of the PLED device

The nanoparticles of  $\text{TiO}_2$  were prepared through sol gel method with titanium tetra ethoxide, TEOT (99%, supplied by Aldrich Chemical) as starting solution.  $\text{TiO}_2$  nanoparticles were synthesized by controlling hydrolysis of TEOT in ethanol. Firstly, three different bottles of 5.0 mL of ethanol was mixed with 0.01 mL of three variations molar of KCl. The molars are  $4 \times 10^{-8}$ ,  $8 \times 10^{-8}$  and  $13 \times 10^{-8}$  for will be categorized as T1, T2 and T3. Then, 0.0425 ml TEOT solution was dropped wisely into each of the ethanolic solution with constant stirring at room temperature for two and a half hours. After two and half hours of stirring, a clear, transparent solution was obtained. The solutions were prepared in a glove box at a room temperature under nitrogen atmosphere and the humidity was kept below 12%. The solution was then deposited on the ITO coated glass substrate with sheet resistance of  $5 \Omega/\text{m}^2$  using spin coating technique. The typical spinning speed and spinning time used were 3000 rpm and 40 s, respectively. The organic solvent was removed by annealing the film at  $200^\circ\text{C}$  for 24 hours. The emitting material, PDPV with a weight of 10 mg or 12 mg was dissolved in 1 mL of toluene each was then deposited on the ITO/ $\text{TiO}_2$  structure using spin coating technique and at the same spinning speed and spinning time. An aluminum layer as cathode was deposited onto the emitting layer through a mask by electron gun evaporation technique from a Molybdenum crucible at a chamber pressure of  $2.5 \times 10^{-5}$  mbar, yielding active areas of  $0.71 \text{ cm}^2$ . The current-voltage of the device was measured using Keithley 238 source measure unit. The  $\text{TiO}_2$  films were also fabricated by the same method on Si wafer. The thicknesses of the buffer layers were measured by Filmetric F50 Thin Film Mapping System while the surface morphology of the film was recorded at the area  $7000 \text{ nm} \times 7000 \text{ nm}$  using an atomic force microscopy, AFM.

## RESULTS AND DISCUSSION

The nanoparticles  $\text{TiO}_2$  layer has been successfully deposited onto the ITO glass substrate to serve as hole injection layer (HIL). Fig. 2 shows the current-voltage ( $I$ - $V$ ) curves of PLED devices with and without  $\text{TiO}_2$  buffer layers. The  $I$ - $V$  curve is the first indicator to determine whether the device is able to emit light or not. The device that shows rectifier diode behaviour is able to produce light. All the PLED devices showed

rectifier diodes. The turn-on voltage could not be determined directly from the  $I$ - $V$  curve. Most researchers determine the turn-on voltage using a tunneling model of the Fowler-Nordheim theory [7]. In this model the tunneling current,  $I$  can be estimated by the equation:

$$I \propto F^2 \exp\left(\frac{-b}{F}\right) \quad (1)$$

where  $F$  is the external electric field and  $b$  is a parameter that depends on the barrier shape. The data from  $I$ - $V$  curves were used to plot  $\ln(I/F)$  versus  $1/F$ . The turn-on voltages were then estimated from these plots. It was found that the turn-on voltage of the device without  $\text{TiO}_2$  buffer layer was 8.0 V, while the device with  $\text{TiO}_2$  buffer layer turn-on at 5.0 V for T1 and T2 while T3 is at 6.0 V. As expected, the device with  $\text{TiO}_2$  has a lower turn-on voltage as the buffer layers has an effect to improve the attribution of holes, leading to more balanced electrons and holes within the recombination zone [8-12].

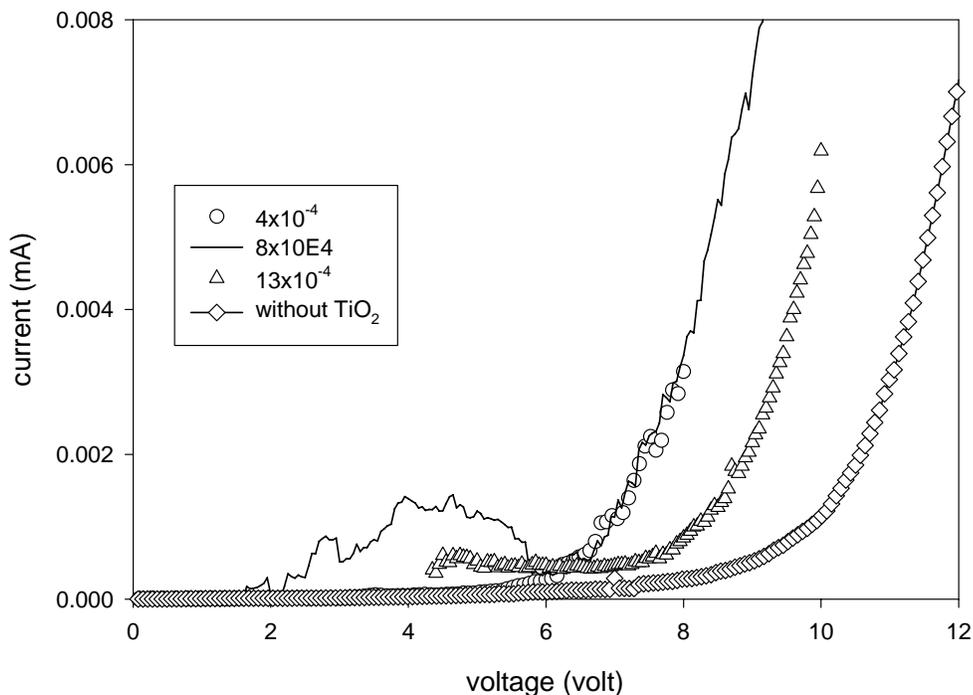


Figure 2: Current-Voltage ( $I$ - $V$ ) characteristic of the PLED devices with 10 mg/ml PDPV

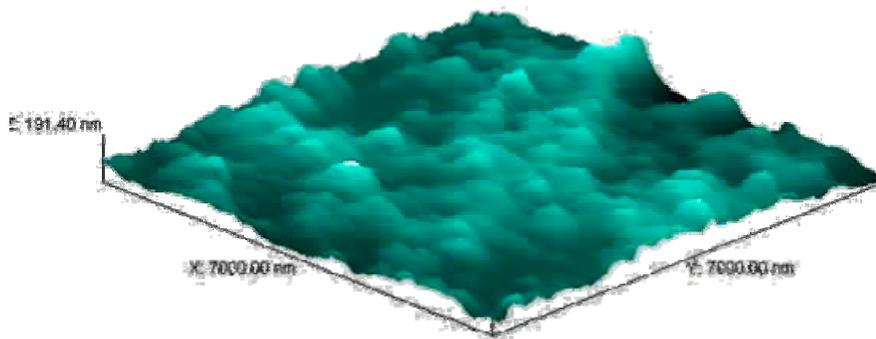
The thicknesses of the HIL layers that were measured by thin film mapper are 8.0 nm, 7.7 nm and 7.0 nm for T1, T2 and T3 respectively. The recent studies showed that the hole injection barriers through the interfaces of ITO/ $\text{TiO}_2$  have almost the same values independent of HIL layer thickness [13]. Our experiment shows that the small

increments of buffer thickness are independent towards turn-on voltage. TiO<sub>2</sub> nanoparticles thin films were deposited on the Si substrates using spin coating technique. The morphology of the TiO<sub>2</sub> nanoarticles thin film was analyzed using Atomic Force Microscopy (Fig. 2). The AFM images of the films on silicon wafer were recorded at the area of 7000 nm × 7000 nm shows that the spikes are dependent to the molarity of the KCl stabilizer. The surface shows a small quantity of spikes, a few nanometer heights on bare substrates surface. It is obvious that that the presence of the TiO<sub>2</sub> spikes can result in an inhomogeneous distribution of the electric field within the organic layers [14-15]. It is believed that the spikes improving the contact with the polymer surface.

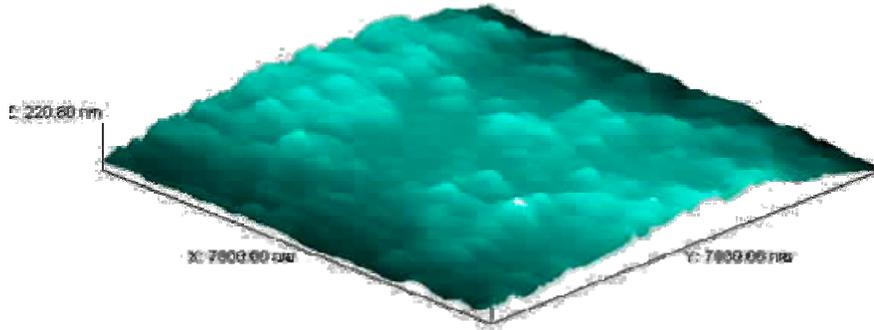
The results showed that higher molarity of PDPV will influence the device turn-on voltage. From Fig. 4 we can assume that by increasing the barrier height should lead to a higher turn-on voltage [7]. From Fowler-Nordheim equation,  $I$  can be estimated by equation:

$$I \propto \exp\left(\frac{-\gamma\phi^{\frac{3}{2}}}{V}\right) \quad (2)$$

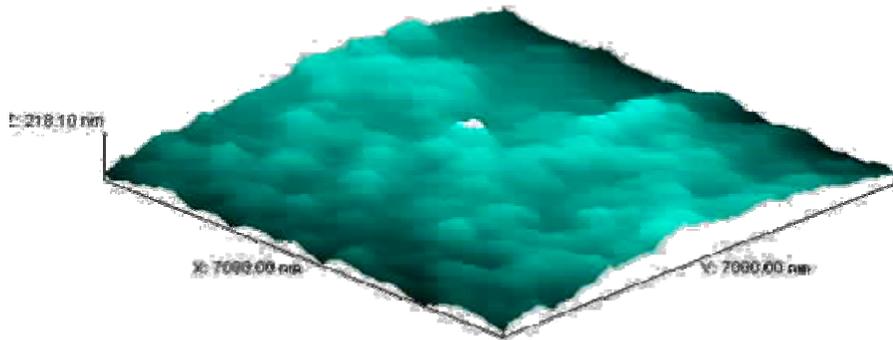
where  $V$  is the applied bias,  $\phi$  is the barrier height, and all the prefactor have been gathered into a single constant  $\gamma$ . So when the barrier height is increased, the turn-on will increase almost double.



(a)



(b)



(c)

Figure 3: AFM images obtained over an area of  $7000 \text{ nm} \times 7000 \text{ nm}$  for  $\text{TiO}_2$  layer with different KCl molar, (a)  $4 \times 10^{-4}$ , (b)  $8 \times 10^{-4}$  and (c)  $13 \times 10^{-4}$

Fig. 5 shows a schematic energy band diagram energy band to explain the role of  $\text{TiO}_2$  in the tunneling effect that has reduced the turn-on voltage. The p-type ITO injects holes as the p-type  $\text{TiO}_2$  injects electron toward each other as the current flows through the device. The electron-hole exchange between the films caused an internal electric field between the ITO- $\text{TiO}_2$  films. The internal electric field will act as a barrier that will block the hole injecting into the polymer through the  $\text{TiO}_2$ . After sometimes, the

current will force the holes injecting through the internal electric field barrier. Once the hole tunnels through the barrier the n-type TiO<sub>2</sub> thin films will immediately injects the hole into the  $\pi$  HOMO level of PDPV. Meanwhile, electrons are injected from Al cathode into the  $\pi^*$  orbital of the LUMO level of the PDPV. These electrons are then moving toward the ITO anode in the opposite direction of the holes. During the travel, each pair of electron and hole recombines to form exciton, a neutral excited state in the PDPV layer. This excited state decays and then generated of the light. With the presence of TiO<sub>2</sub> nanoparticles thin films, the hole-electron recombination were optimize and lead to low turn-on voltage [8-14].

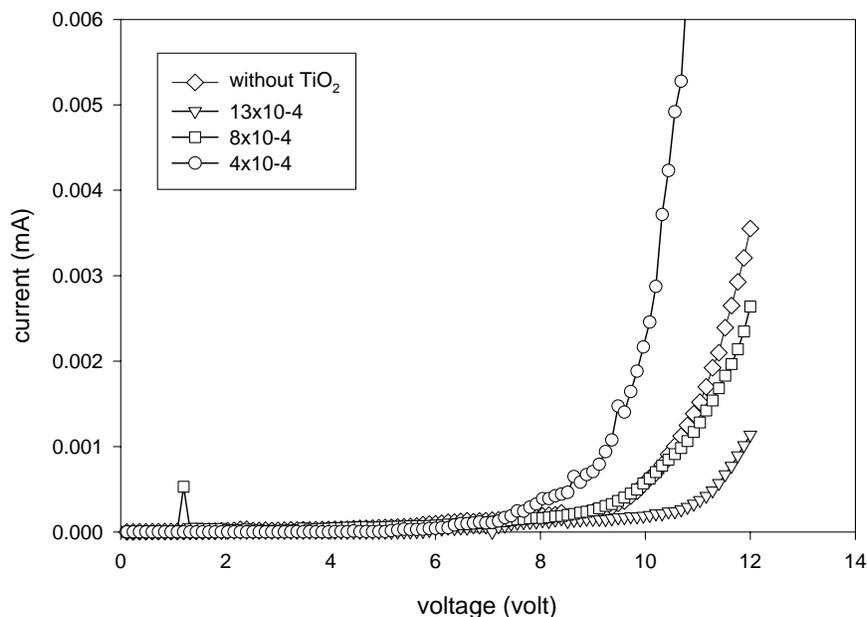


Figure 4: Current-Voltage (I-V) characteristic of the PLED devices with 12 mg/ml PDPV

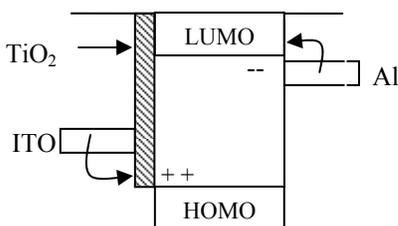


Figure 5: Schematic of injection carriers in the device

## CONCLUSION

The ITO/TiO<sub>2</sub>/PDPV/Al structured of the PLEDs device has been successfully fabricated. It was found that the TiO<sub>2</sub> hole injection layer with a thickness 8.0 nm with  $4 \times 10^{-4}$  molar of KCl give us the lowest value of PLED turn-on voltage.

## ACKNOWLEDGEMENT

This work has been carried out with the support of the Malaysian of Science, Technology and Innovation, under the IRPA grant 03-02-006-SR007/04-04.

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