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REDUCTION OF TURN-ON VOLTAGE IN POLYMER ORGANIC LIGHT-EMITTING DIODE USING NANOPARTICLES TiO_2 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 applications. We had fabricated the nanoparticles TiO_2 thin film between ITO and PDPV in Al/PDPV/ITO structure as a hole injection layer. The sol gel method synthesized of TiO_2 thin film was deposited using spin coating technique. It was found that TiO_2 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 plat 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_2 layers between electrodes and other organic layers in the device structured. This paper reports the effect of using TiO_2 nanoparticles as buffer layer on the turn-on voltage of the devices. We choose TiO_2 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_2 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_2 as titanium dioxide as a hole injection layer and Al is aluminium thin film as cathode.

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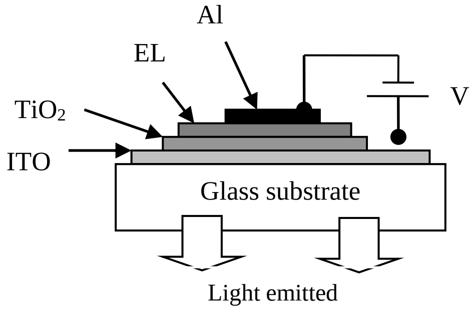

Figure 1: Structure of the PLED device

The nanoparticles of TiO_2 were prepared through sol gel method with titanium tetra ethoxide, TEOT (99%, supplied by Aldrich Chemical) as starting solution. 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 4×10^{-8}, 8×10^{-8} and 13×10^{-8} for will be categorized as T1, T2 and T3. Then, 0.0425 ml TEOT solution was dropped wisely into each of the ethanoloic 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 Ω/m^2using 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 200^0C 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/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 2.5×10^{-5} mbar, yielding active areas of 0.71 cm^2. The current-voltage of the device was measured using Keithley 238 source measure unit. The 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 nm × 7000 nm using an atomic force microscopy, AFM.

RESULTS AND DISCUSSION

The nanoparticles 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 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

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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:

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

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 TiO_2 buffer layer was 8.0 V, while the device with 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 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].

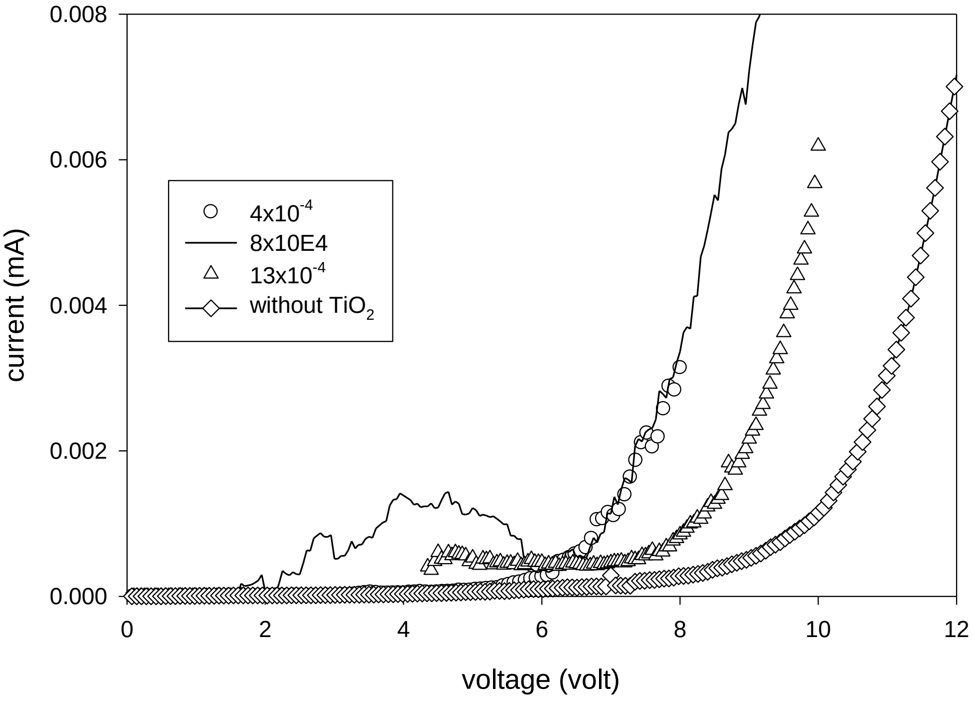


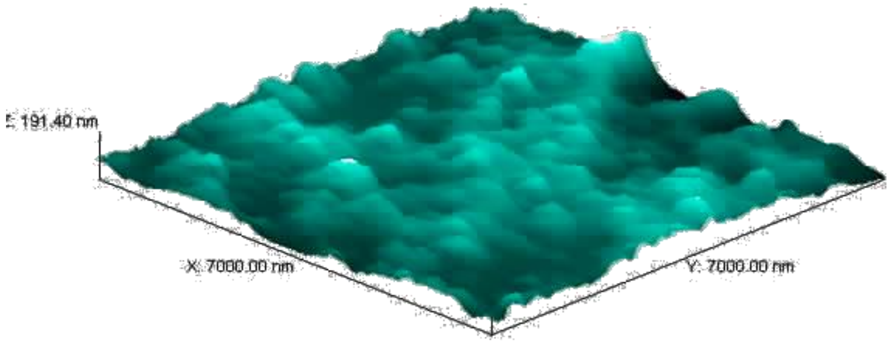
Figure 2: Current-Voltage (I-V) characteristic of the PLED devices with 10 mg/ml PDPV

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/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_2 nanoparticles thin films were deposited on the Si substrates using spin coating technique. The morphology of the TiO_2 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_2 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:

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

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



(a)

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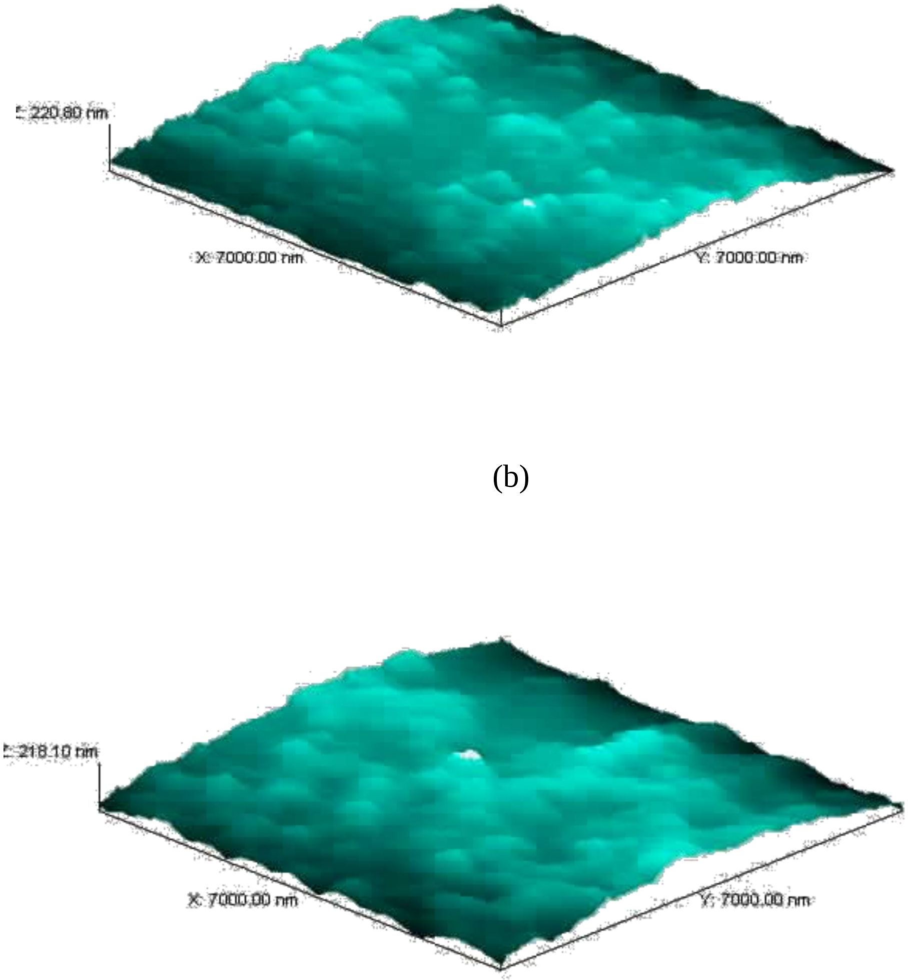

(b)

(c)

Figure 3: AFM images obtained over an area of 7000 nm × 7000 nm for TiO_2 layer with different KCl molar, (a) 4×10^{-4}, (b) 8×10^{-4} and (c) 13×10^{-4}

Fig. 5 shows a schematic energy band diagram energy band to explain the role of TiO_2 in the tunneling effect that has reduced the turn-on voltage. The p-type ITO injects holes as the p-type 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-TiO_2 films. The internal electric field will act as a barrier that will block the hole injecting into the polymer through the 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_2 thin films will immediately injects the hole into the π HOMO level of PDPV. Meanwhile, electrons are injected from Al cathode into the π* 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 exited state in the PDPV layer. This exited state decays and then generated of the light. With the presence of TiO_2 nanoparticles thin films, the hole-electron recombination were optimize and lead to low turn-on voltage [8-14].

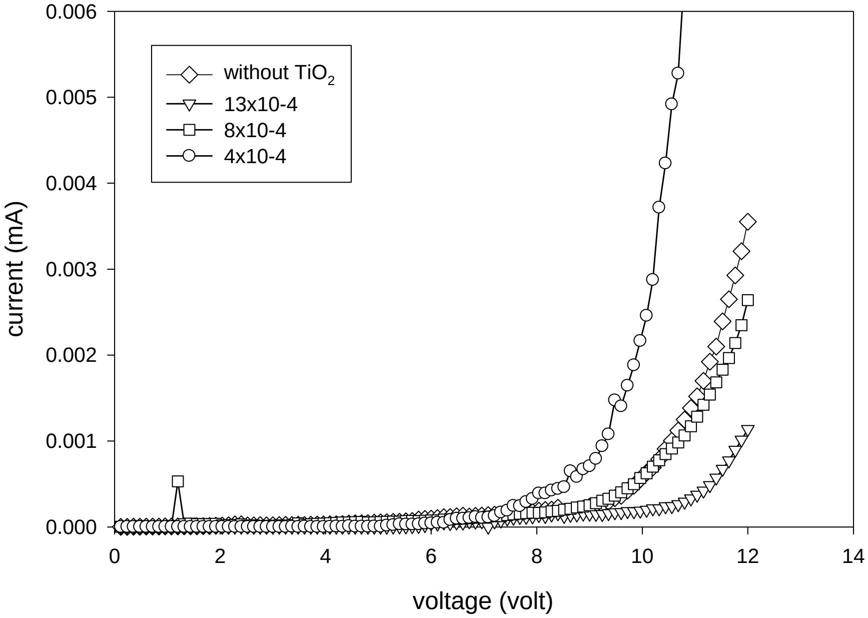

Figure 4: Current-Voltage (I-V) characteristic of the PLED devices with 12 mg/ml PDPV

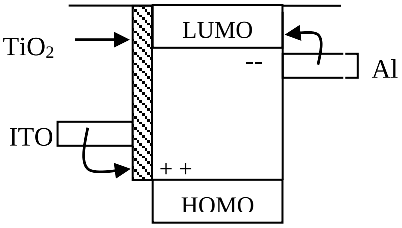

Figure 5: Schematic of injection carriers in the device

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CONCLUSION

The ITO/TiO_2/PDPV/Al structured of the PLEDs device has been successfully fabricated. It was found that the TiO_2 hole injection layer with a thickness 8.0 nm with 4×10^{-4} molar of KCl give us the lowest value of PLED turn-on voltage.

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REFERENCES

[1] Furong Zhu, Huan, C.H.A., Keran Zhang and Wee, A.T.S. (2000); Investigation of annealing effects on indium tin oxide thin films by electron energy loss spectroscopy, *Thin Solid Films*, Vol. **359**, pp. 244-250.

[2] Li, C.N., Kwong, C.Y., Djurisic, A.B., Lai, P.T., Chui, P.C., Chan, W.K., Liu, S.Y. (2005): Improved perfomances of OLEDs with ITO surface treatments, *Thin Solids Film*, Vol. **477**, pp. 57-62.

[3] Buwen, X., Yafeng, S., Meng, M. and Chuannan, L. (2005): Enhancement of hole injection with an ultra-thin Ag_2O modified anode in organic light-emitting diodes, *Microelectronics Journal*, Vol. **36**, No. 2, pp.105-108

[4] Shengwei Shi and Dongge Ma, (2005); A pentacene-doped hole injection layer for organic light-emitting diodes, *Semiconductor Science and Technology*, Vol. **20**, pp. 1213-1216.

[5] Yang, Y., Westerweele, E., Zhang, C., Smith, P. and Heeger, A.J. (1995); Enhanced perfomance of polymer light-emitting diodes using high-surface area polyaniline network electrodes, *Journal of Applied Physics*, Vol. **77**, pp. 694-698.

[6] Chengfeng Qiu, Haiying Chen, Zhiliang Xie, Man Wong and Hoi Sing Kong, (2002); Praseodymium oxide coated anode for organic light-emitting diode", *Applied Physics Letters*, Vol. **80**, pp. 3485-3487.

[7] Parker, I.D. (1994); Carrier tunneling and device characteristics in polymer light-emitting diodes. *Journal Of Applied Pysics*, **75**, pp.1656-1666.

[8] Ding, X.M. (2000); Modification of the hole injection barrier in organic light–emitting devices studied by ultraviolet photo electron spectroscopy, *Appiled Physics Letters*, Vol. **76**, pp. 2704-2706.

[9] Yudi Gao, Liduo Wang, Deqiang Zhang, Lian Duan, Guifang Dong & Yong Qiu. (2003); Bright single-active layer small-molecule organic light-emitting diodes with a polytetrafluoroethylene barrier. *Applied Physics Letters* **82**, pp. 155-157.

[10] Deng, Z.B. and Ding, X.M. Enhanced brightness and efficiency in organic electroluminescent devices using SiO_2 buffer layer", *Applied Physics Letters*, Vol. **74**, pp. 2227-2229.

Corresponding Author: mms@pkrisc.cc.ukm.my

[11] Huang, Z.H., Zeng, X.T., Kang, E.T., Fuh, Y.Y. and Lu, L. (2005); Ultrathin sol-gel titanium oxide hole injection layer in OLEDs, *Surface & Coating Technology*, Vol. **198**, pp. 357-361.

[12] Deng, Z.B., Ding, X.M., Liao, L.S., Hou, X.Y. and Lee, S.T. (2000); The interface analyses of inorganic layer for organic electroluminescent devices, *Displays*, Vol. **21**, pp. 79-82.

[13] Tadayyon, S.M., Grandin, H.M., Griffiths, K., Norton, P.R., Aziz, H. and Popovic, Z.D. (2004); CuPc buffer layer role in PLED performance: a study of the interfacial band energies, *Organic Electronics*, Vol. **5**, No. 4, pp. 157-166.

[14] Furong Zhu, Beeling Low, Keran Zhang and Soojin Chua, (2001); Lithium-fluoride-modified indium tin oxide for enhanced carrier injection in phenyl-substituted polymer electroluminescent devices, Appl. Phys. Lett. **79(8)**, pp. 1205-1207.

[15] Zhang Zhi Feng, Deng Zhen-Bo, Liang Chun-Jun, (2003); Organic light-emitting diodes with a nanostructured TiO_2 layer at the interface between ITO and NPB layers, *Displays*, Vol. **24**, No. 4-5, pp. 231-234.

Corresponding Author: mms@pkrisc.cc.ukm.my