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Degradation in Organic Light Emitting Diodes

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***Abstract*—**The objective is to fabricate organic light emitting diode and to study its degradation process in atmosphere condition in which PFO as an emitting material and PEDOT:PSS as a hole injecting material were used on ITO substrate. Thus degradation process of the OLED was studied upon its current-voltage characteristic. By fabricating this OLED and obtaining blue light and analysis of current-voltage characteristic during the time after fabrication, it was observed that the current of the OLED was exponentially decreased. Current reduction during the initial hours of fabrication was outstanding and after few days its reduction rate was dropped significantly, while the diode was dying.

***Keywords*—**OLED, Degradation, Dark spot.

I. Introduction

ORGANIC light emitting diodes have limited life time and their stability is affected by the numerous factors. These factors can be divided into two groups: Intrinsic factors and environmental factors. Intrinsic factors playing role in OLED degradation are as follows:

Excited state formation is intrinsic to the operation of OLEDs. Irreversible chemistry of the excited states can remove emissive species from the device. Even worse, these reaction products may form quench centers for excitons formed on nearby unaffected site. This reaction can be with elements available in their environment such as the adjacent organic layers [1, 2]. Crystallization of organic materials is another factor of degradation of organic layers coming from low glass transition temperature and being effected by heat coming from injection barrier specially anode injection barrier [2]. On the other hand, organic materials are softer and have weaker molecular bonds in comparison with non-organic materials and ion movement in its layers is easier. Mobile ions such as In, Sn, Mg, … that penetrate into layers through electrodes or contaminations during the device construction, affects applied effective field inside the device and therefore diode operation [3].

But the more important factors playing role in the actual life time of OLED are environmental factors such as light, oxygen and humidity. Organic materials in excited state are easily reacted with oxygen and humidity and new chemical structures are produced and its emitting property is failed in these regions. OLED which is exposed to atmosphere conditions directly and without encapsulation, has limited life time. Operating OLED in air resulted in a 99% loss of EL intensity in as little as 150 min [4]. Decrease of current and increase of threshold voltage are observed in degradations of OLEDs [5, 6]. One of the factors of OLED degradation is current decreasing in a constant biased voltage versus time which this matter is resulted by evolution of non-emissive region, or dark spots, and so decrease of the device area [7].

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II. Experimental

In order to fabricate organic light emitting diode, ITO on glass substrate as transparent anode metal with thickness of 125 nm, resistant of 12 ohm/sq. and size of 1.2 mm ×1.2 mm which purchased from Merck Company was used. ITO surface was ultrasonically cleaned in 2% soap and water solution with temperature of 60° C to 80° C, acetone, methanol with temperature of 60° C, isopropanol with temperature of 60° C respectively, each for five minutes. After cleaning, PEDOT:PSS as a hole injecting layer and PFO solution with 10 mg/ml concentration in toluene solvent was spin coated with speed of 3000 rpm and time of 60 sec. and 30 sec., respectively. PEDOT:PSS material with trademark of TPCH8000 was purchased from Bayer Company and PFO was purchased from Sigma Aldrich Company. Deposition of Al as cathode was carried out by method of thermal evaporation in vacuum of 5×10^{-5} mbar through a shadow mask. Active area of each diode was 1.5×3 mm^2.

Diode voltage-current characteristic was measured by a source measure unit Keithley 238. The applied voltage was a step function with 1 volt step value and approximate 1 minute step delay. Images of samples were taken by Scanning Electron Microscopy named as VEGA-II Tescan.

III. Results and Discussions

A. Voltage-current characteristic of diode with the structure of ITO/PEDOT:PSS/PFO/Al.

Because of difference between ionization energy of PFO, 5.2eV, and work function of PEDOT:PSS, 5.8eV, the hole current is limited by injection [8]. Also since energy difference between work function of Al, 4.3eV, and electron affinity of PFO, 2.85eV, was much, therefore non-ohmic junction is made [9]. Thus current in the analyzed diode with the structure of ITO/PEDOT:PSS/PFO/Al is injection limited current [10]. Band diagram of the diode is depicted in Fig. 1.

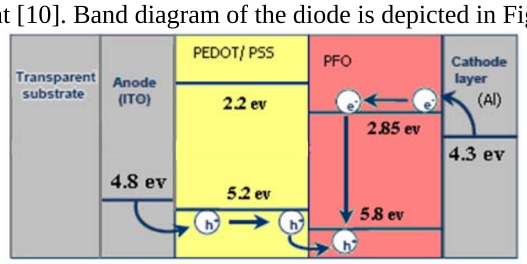


Fig. 1 Band diagram of diode with the structure of ITO/PEDOT:PSS/PFO/Al

Fig. 2 shows characteristic curve of the diode measured immediately after fabrication. In currents under about 10 volts, low current is passed through the device within thermionic emission over injection barrier. By increasing voltage more than about 10 volts, the width of injection barrier is decreased and current is passed through tunneling [11,12]. In this case, in addition to current is limited by injection, other mechanisms such as SCLC [11,12] and TCLC [11] are played role in determination of current value.

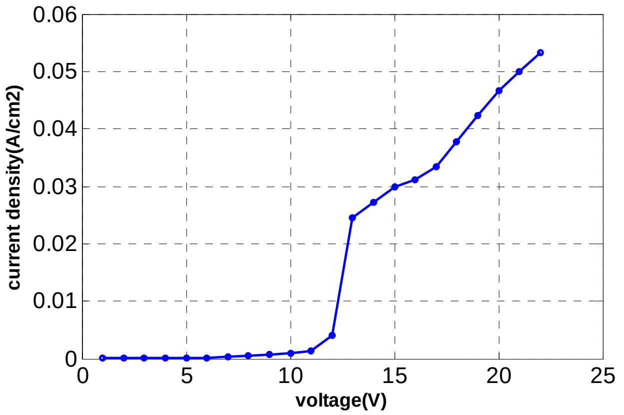


Fig. 2 J-V characteristic curve of diode with structure of ITO/PEDOT:PSS/PFO/Al In the first measurement after fabrication

B. Analysis of degradation process of diode with structure of ITO/PEDOT:PSS/PFO/Al

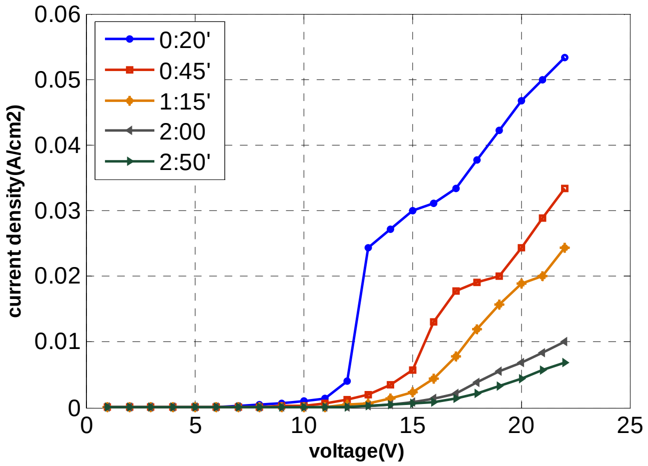


Fig. 3 J-V characteristic of OLED with structure of ITO/PEDOT:PSS/PFO/Al during the time after fabrication which has been measured in atmosphere condition

Electrical aspect of degradation process was analyzed by measuring J-V characteristic of device during the time after fabrication and in the atmosphere condition, which is depicted in Fig. 3. In order to prevent high voltage effect on the degradation of device, voltage range was selected between 0 to 22 volts which cause the maximum current density of 0.054 A/cm^2.As this figure shows, by passing time, current density is decreased and threshold voltage is increased.

One of the criteria of organic diode degradation is increase of voltage drop of device in a constant current or decrease of current in a constant applied voltage and this is related to resistivity increase of organic layers [7]. To analyze degradation of this diode, its current curve versus time in a constant voltage is measured and shown in Fig. 4. The main figure has logarithmic axis and the linear form of this figure in initial times of testing is shown as an inset.

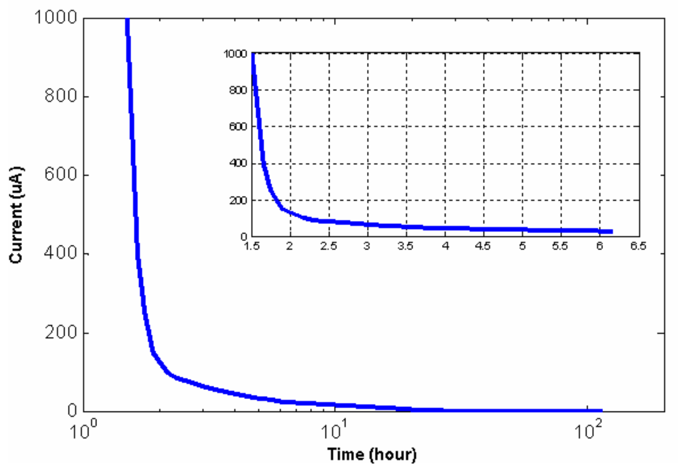


Fig. 4 Current- time characteristic of OLED with structure of ITO/PEDOT:PSS/PFO/Al in voltage of constant biased of 17 volts which has been measured in atmosphere condition

As it is observed in Fig. 4, current decrease process is exponential. Current deduction during the initial hours of fabrication is outstanding in such a way that initial and major drop is taken place during the first five to six hours. Then by passing time its reduction rate is declined and after few days its reduction rate was dropped significantly. At this time diode is reached to the end of its lifetime.

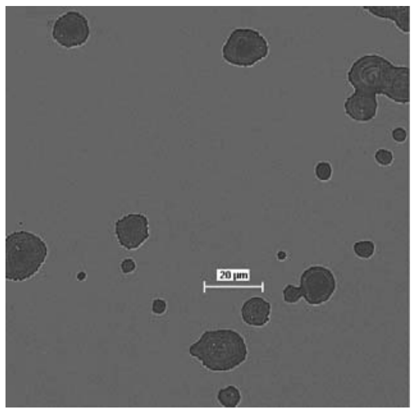


Fig. 5 SEM image of defected ITO after diode fabrication and testing in atmosphere condition

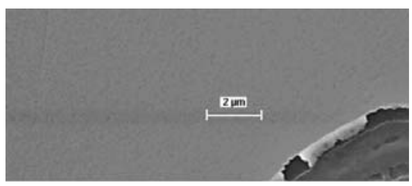


Fig. 6 SEM image of defected ITO of Fig. 5 in larger scale

One of the symbols of OLED degradation is dark spots. For any reason in which dark spots are appeared, their size shall be gradually increased and in addition to effecting on cathode metal and emitting layer, they impact on lower organic layers and ITO surface [2]. After fabrication of OLED, SEM images were taken from ITO surface on which diode was fabricated. SEM images of a sample of ITO on which diode was fabricated and tested in atmosphere condition, are shown in Fig. 5.

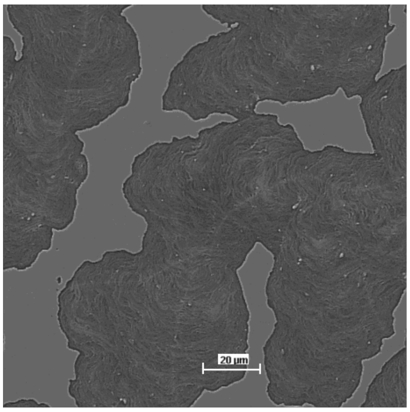


Fig. 7 SEM images of fully defected ITO due to voltage

As we found from Fig. 5, after fabrication, testing and full degradation of device in atmosphere condition, defects are remained on ITO surface. Fig. 6 shows these defects in larger scale. Increasing the applied voltage causes dark spots due to high local electric field formation [7].

In addition to gradual defect of device in atmosphere condition, by increasing voltage up to voltages more than normal operating voltage, the device becomes out of order and defects on ITO have been expanded and have covered the most area of device. In the other words, increase of voltage and heating device accelerate defect process. Fig. 7 shows SEM images of fully defected ITO due to voltage.

C. Analysis of injection barrier effect on operation and OLED degradation

In order to analyze injection barrier effect on operation and OLED degradation, device with the structure of ITO/PEDOT:PSS/PFO/Au was also constructed.

This device due to big electron injection barrier between work function of Au, 5.1eV, and LUMO energy level in PFO, is unipolar and conducts just holes [8, 10]. Even thought in the case PFO was doped with BT, a phosphoresce material combination of 95% of PFO and 5% of BT was expected to emit green light , due to unipolar nature of this structure, no light was emitted.

Also due to the same reason of large barrier, its current in comparison with cathode Al, becomes less significantly.

In analysis of the device degradation with Au cathode, its J-V curves which are shown in Fig. 8, are measured in two cases of PFO without impurity and doped PFO with BT during the time after fabrication in atmosphere conditions. Current-time curves of these diodes are shown in Fig. 9.

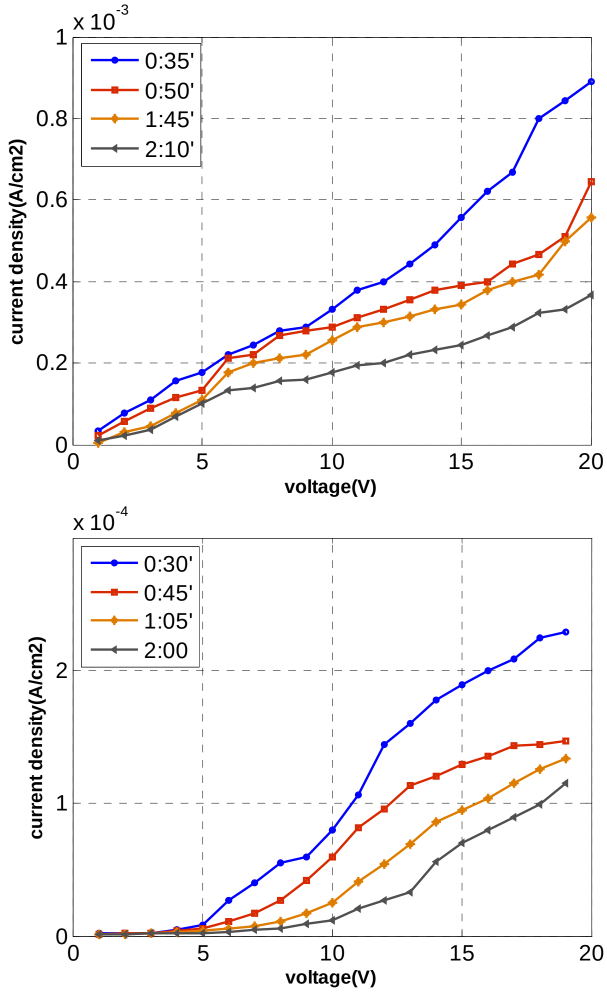
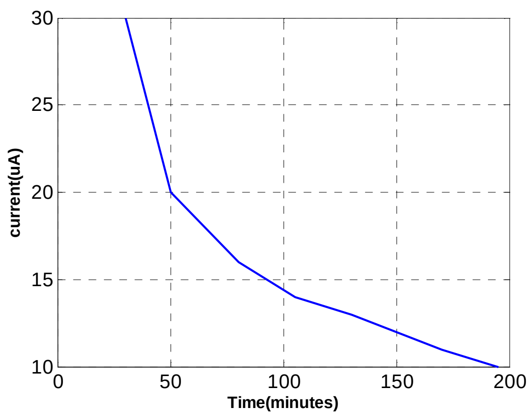


Fig. 8 J-V characteristic curves of OLED with the structure of ITO/PEDOT:PSS/PFO/Au during time after fabrication with PFO without impurity (top) and PFO with BT (bottom) which were measured in atmosphere conditions



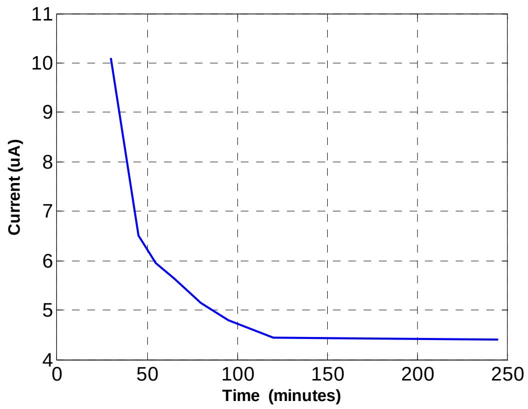


Fig. 9 Current-time characteristic curves of OLED with the structure of ITO/PEDOT:PSS/PFO/Au in constant biased voltage with PFO without impurity (top) and PFO with BT (bottom) which were measured in atmosphere conditions

Curves of figures 8 and 9 indicate that such as the previous structure (Al cathode), by passing time, current density is decreasing in atmosphere conditions and Threshold voltage is increasing. Also this current decrease is exponential and so independent of injection barrier. On the other hand, manner of degradation of OLED with this structure depends on degradation of organic layers.

D. Reasons of OLED degradation with structure of ITO/PEDOT:PSS/PFO/metal in brief

Defects can be observed on SEM images. Since, by increasing voltage up to voltages more than normal operating voltage, defects on ITO have been expanded, we can conclude, temperature and high local electric field in the surface or unsmooth inter-layer points of the device, may cause defects during diode operation and therefore cause diode failure. This concept is also improved by Burrows et. al. [7].

Additionally, the other reason of these defects on ITO surface can be effect of dark spots which is also because of high current and high electric field in mentioned area [6, 7]. These points shall be gradually become larger during the device operation and remain some effects on diode layers [2] such as ITO surface which the effects are apparently observed.

Organic materials can react with environmental elements especially in their excited state. The reaction even can be with its adjacent layers for instance PFO reaction with PEDOT:PSS in these two layer interface. This matter causes doping decrease of PSS in PEDOT:PSS layer. Therefore, barrier between these layers are increased and current in the device are decreased [1].

The major and important reason of OLEDs is the exposure to air and their reaction with oxygen and humidity of air. This action in warmer area and dark spots is more [6] causing its resistance increase during the time and therefore its current is decreased.

IV. Conclusion

OLED with structure of ITO/PEDOT:PSS/PFO/Al in atmosphere condition shows rapid degradation rate, thus current density is decreased and threshold voltage is increased during the time. In this diode decrease of current versus time is exponential and outstanding during the initial hours after fabrication.

In the device fabricated with Au cathode, the same degradation process was observed. This matter indicates that manner of degradation of OLED is independence of injection barrier.

The major reason of OLED degradation is the reaction of organic material with oxygen and humidity of air in atmosphere conditions. The defects of layers start from the specific points and become larger gradually and therefore, their resistance shall be increased and the device current shall be deceased until the organic layers are fully defected and the device current is dropped significantly.

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